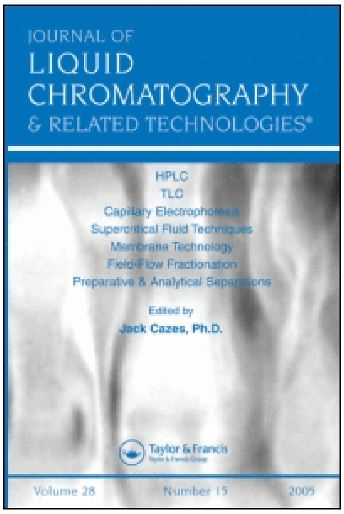

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SILYLATION OF THE SILICA SURFACE
A REVIEW

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ABSTRACT

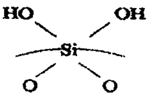
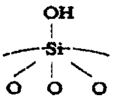
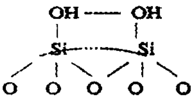
Silylated silica surfaces have found many applications in the field of analytical chemistry (HPLC, Ion Exchange Chromatography, Size Exclusion Chromatography, GC), synthetic chemistry (heterogeneous catalysts, phase transfer catalysts), biochemistry (enzyme immobilization, affinity chromatography) and industries (composites, high-tech materials, semiconductor devices).

In all cases, the knowledge of their chemical composition and surface characteristics is of great importance for the understanding and eventual improvement of their performance.

This review presents a general description of the silica surface and a summary of the different modification techniques that have been developped to silylate oxide surfaces. The chlorosilylation of the silica surface (in liquid and gaseous phase) and the modification with aminosilanes are discussed in more detail, emphasizing the analysis techniques and skills that enable researchers to get a more profound insight into the reaction mechanisms and the nature and concentration of the created surface groups.

Table 1

Surface Silanol Types with their ^{29}Si CP MAS NMR and FTIR Peak Positions and Names

			
	Geminal	**Isolated**	**Vicinal**
Si-NMR	Q2 -94 ppm	Q3 -100 ppm	Q3 -100 ppm
FTIR	3743 cm^{-1} free	3743 cm^{-1} free	3660 cm^{-1} bridged

1. The Surface of Silica - Quantification of the Silanol Types as a Function of Temperature

The ultimate particles which make up the silicas can be regarded as polymers of silicic acid, consisting of interlinked SiO_4 tetrahedra. At the surface, the structure terminates in either a *siloxane group* (≡Si-O-Si≡) with the oxygen on the surface, or one of several forms of *silanol groups* (≡Si-OH). The silanols can be divided into *isolated* groups (or *free silanols*), where the surface silicon atom has three bonds into the bulk structure and the fourth bond attached to a single OH group, and *vicinal silanols* (or *bridged silanols*), where two single silanol groups, attached to different silicon atoms, are close enough to hydrogen bond.

A third type of silanols, *geminal silanols*, consist of two hydroxyl groups, that are attached to one silicon atom. The geminal silanols are too close to hydrogen bond to each other,[2] whereas the free hydroxyl groups are too far separated. These different silanol types, together with their infrared and ^{29}Si NMR attributes are shown in Table 1.

Since silanols play an important role in all surface modifications, a thorough understanding of the absolute number of silanols and the relative distribution of the silanol types is very important. A very large number of publications has appeared on the distribution of these various silanol types as a function of pretreatment temperature of the silica. We have recently evaluated the most important of these models[1] and have come to an average distribution of silanol types, shown in Figure 1.

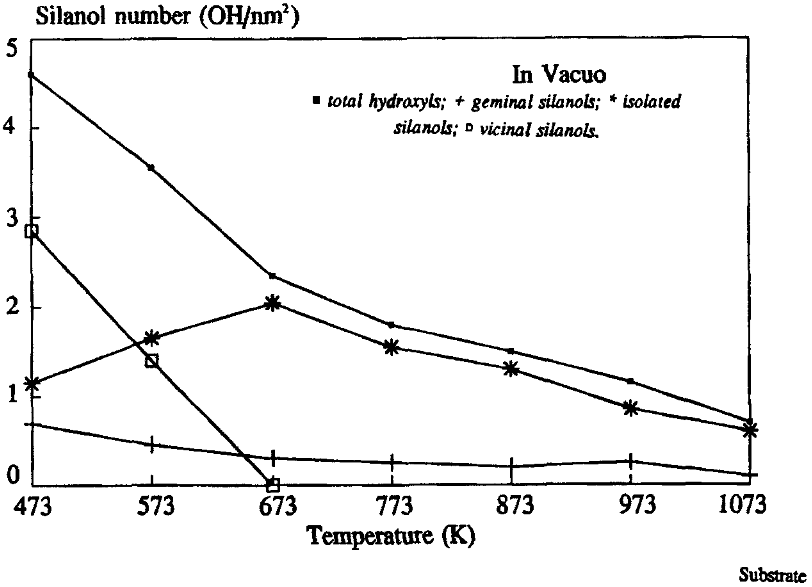


Figure 1. Silanol type distribution as a function of pretreatment temperature. In vacuo.

2. Silylation of the Silica Surface: Modification Procedures

In the selection of a chemical modification procedure, two criteria have to be considered.

(i) the aimed coating morphology; and

(ii) the scale on which the modification has to be performed.

The coating morphology includes layer thickness (mono- or multi-layer), the modification density (molecules/nm²), the orientations of the surface molecules, and the type of interaction of the coating layer with the surface (relative amount physisorption/chemisorption).

The procedures used for the chemical modification of silica will be discussed using these criteria. This survey is restricted to the preparation of chemically modified silicas, used as a base material in the above-cited applications. Procedures are ordered according to the possibility to control the ultimately formed layer.

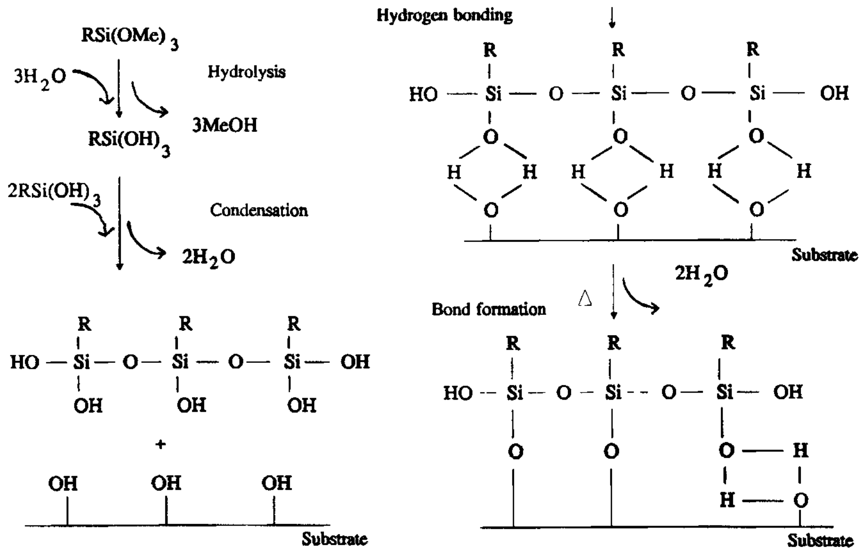


Figure 2. Mechanism of silane deposition in aqueous solvent.

Sol-gel

The incorporation of organofunctional groups on the silica surface may be effected during the synthesis of the silica material. The addition of organofunctional alkoxysilanes to the TEOS (tetraethoxysilane) solution in the sol-gel process, produces functionalized silica gels. This procedure does not allow a careful control of the resultant surface morphology. Since the relative amounts of silane and TEOS are the only variable parameters, neither layer thickness, nor modification density can be precisely tuned. This results in an irreproducible functionalization of the surface.

Aqueous Solvent

The preparation of organofunctional silica gels on an industrial scale is performed by liquid phase reaction. As a solvent, water, a water/ethanol or water/acetone mixture is used. Chlorosilanes or alkoxysilanes are used for this type of modification.

In the aqueous solvent, the silanes undergo hydrolysis and condensation before deposition on the surface[3] (Figure 2). In contact with water, halogen or alkoxy groups are hydrolyzed. The as-formed silanol groups go into hydrogen-bonding interactions with neighbouring hydrolyzed silane molecules and with surface silanol groups. Siloxane bonds are formed, with release of water. The coating molecules are polymerized horizontally as well as vertically. Thus, a three-dimensional polymeric silane network is formed on the silica surface.

The polymerization reactions are hard to control and a layer of unreproducible thickness results. The control is ameliorated with the addition of a variable amount of a polar organic solvent, such as ethanol or acetone. Ethanol/water mixtures in a 70%/30% ratio are commonly used.

Covalent bond formation is not an immediate process. Silane coating layers consist of physisorbed as well as chemisorbed molecules. Physisorbed molecules go into condensation only slowly and chemical stabilization of the coating layer requires a post-reaction curing step. In this step, the modified substrate is thermally treated at temperatures generally in the 353 - 473 °K range.

Organic solvent

If modification with chlorosilanes or alkoxysilanes is performed in completely dry conditions (dry organic solvent, dehydrated surface), hydrolysis is prevented. Chemical bonding with the substrate should result from the direct condensation of the chloro- or alkoxy groups with the surface silanols. From experiments using methoxymethylsilanes, Blitz[2] concluded that this direct condensation does not take place. Post-reaction curing only results in evaporation of the adsorbed molecules. Alkoxysilanes may only bond chemically to the silica surface if water is present at the interface. Thus adsorbed silane molecules are hydrolyzed before reaction with the surface. Hydrolysis, however also causes polymerization and, therefore, non-monolayer coverages are obtained.

Another way to realize the direct condensation is by using ammonia as a catalyst. Blitz and coworkers[5] studied the reactions of methoxymethylsilanes with silica in a dry toluene medium in the presence of ammonia. They found that high-temperature post-reaction curing is unnecessary for silylation to occur on the silica surfaces (either wet or dry) in the presence of ammonia. Monolayer or greater than monolayer surface coverage is obtained when ammonia is present and is about 12 times the surface coverage obtained in the absence of ammonia. In Figures 3 a and b, two possible mechanisms of ammonia catalysis are proposed.[6]

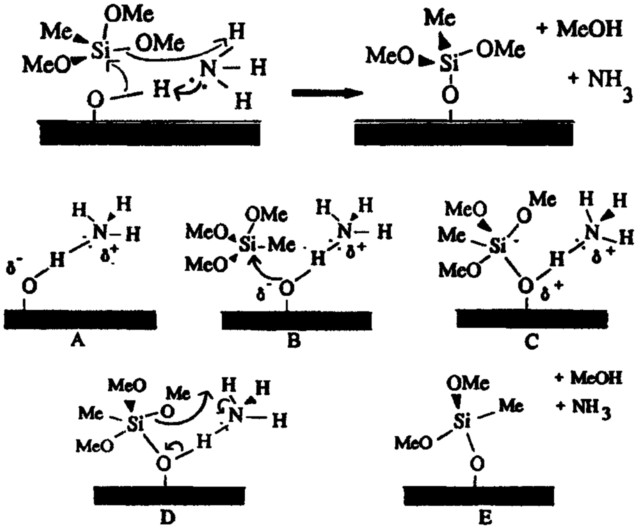


Figure 3. (a) Amine catalysis of silylation reaction, mechanism #1; (b) Amine catalysis of silylation reaction, mechanism #2.

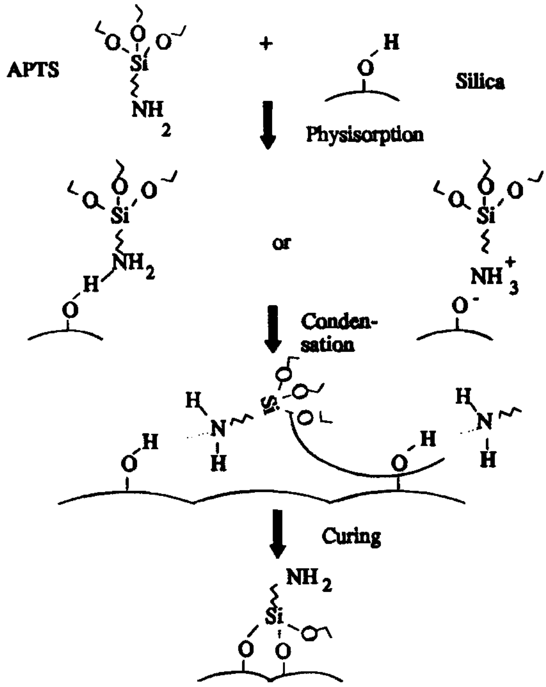


Figure 4. Modifcation of silica gel with APTS.

In the first mechanism (Figure 3a) the transition state involves the formation of a low-energetic six-membered ring. The second mechanism (Figure 3b) proceeds by the formation of a pentacoordinate intermediate, after nucleophilic attack of the ammonia at the silicon atom.

Aminosilanes contain the catalyzing amine function in the organic chain. The reaction of aminosilanes with silica gel in dry conditions is therefore self-catalyzed. They show direct condensation, even in completely dry conditions. Upon addition of the aminosilane to the silica substrate, the amine group may form hydrogen bonds or proton transfer complexes with the surface silanols. This results in a very fast adsorption, followed by direct condensation. This reaction mechanism of APTS (γ-aminopropyltriethoxysilane) with silica gel in dry conditions, is shown in Figure 4. After liquid phase reaction, the filtered substrate is cured in order to consolidate the modification layer.

Self-Assembled Monolayers

Among the liquid phase adsorption procedures, Self-Assembled Monolayers (SAMs) take a special place. This type of monolayer originated as an extension of Langmuir-Blodgett film technology.[7] In this latter technique, highly ordered films of large polar molecules are deposited on flat surfaces. Being obtained as insoluble ordered floating films on the surface of a liquid, Langmuir-Blodgett monolayer films are transferred onto solid supports, from the water-gas interface, by dipping or immersion of the substrate (Figure 5).

In the formation of SAMs, the film-forming molecules order themselves by chemical interaction with neighbouring molecules and with the substrate surface. This technique has been applied for a large variety of modifier/substrate combinations. Various sulphur compounds, such as alkanethiols and (di)sulfides have been deposited on metals such as silver, copper and gold; isocyanides on platinum and carboxylic acids on aluminum oxide and silver oxide.[8] Alkyltrichlorosilanes have been deposited on gold, mica, aluminum, tin oxide and silicon oxide. The latter combination is of interest here.

The main feature of the technique is the deposition of the coating molecules from organic solvent onto a cleaned hydrated surface. As a solvent dicyclohexyl, ethanol, n-hexadecane and n-heptane are used. In a typical synthesis procedure, the silica is first cleaned to remove all trace organic compounds. This cleaning step appears to be crucial in the formation of smooth, complete monolayers, especially on metal surfaces. Cleaning is performed by boiling in nitric acid or hydrogenperoxide/sulphuric acid ('piranha') solution. The cleaning step is followed by a careful rinse with distilled water and drying in a stream of dry nitrogen.

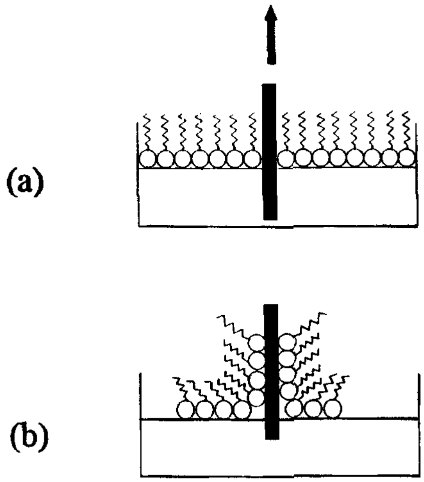


Figure 5. Langmuir-Blodgett film formation on a solid support by transfer of a film at liquid-gas interface (a) to solid-gas (b) interface.

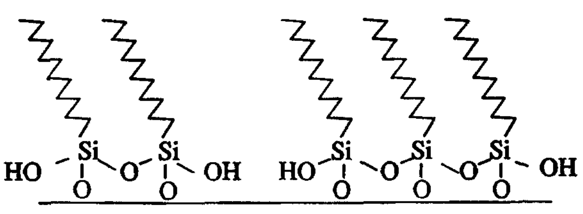


Figure 6. Schematic drawings of self-assembled monolayer (upper) and conventional monolayer. Taken from ref 11, with permission.

The silica may be rehydrated by exposure to air, with controlled humidity, shortly before use. Whereas the modification of flat solid substrates involves an immersion/retraction procedure, this is not possible for powdered substrates such as silica gel. Therefore, these are stirred in the reagent solution, filtered or decanted and rinsed with the pure solvent. Detailed descriptions of the reaction conditions may be found in the literature.[7,9,10]

The SAM is formed by using only the monolayer of surface water on the silica gel. Since no excess water is present, the polymerization reaction is strictly under control. Additionally, the water is present at the place where the surface bond has to be formed.

Thus-formed SAM's are densely packed, ordered films, attached to the surface with chemical bonds. Alkyl chains are aligned paralel in a densely packed fashion. The surface is fully covered, irrespective of the number of hydroxyl groups. Not all silane molecules are covalently linked to the surface. Le Grange et al.[9] evidenced that on a dehydrated surface that was exposed to moisture, 1 in 5 octadecylchlorosilane molecules is bonded to the surface. Due to this dense structure and full surface coverage, this type of layer is clearly different from other wet modification methods. In Figure 6 the structure of a self-assembled monolayer is compared to that of a conventional polymeric layer.

Wirth and Fatunmbi[11] defined the bonding of trifunctional silanes as self-assembly, when the bonding density of functional groups is made to be close-packed, approximately 8 μmol/m^2 (2.2 nm^2/chain). Conventional polymeric phases are no more than 5 μmol/m^2. Because of their close packing, these phases are very well suited for chromatographic separations, since all interference of surface hydroxyls is excluded. In order to avoid over-crowding of the alkyl chains, but to retain the advantages of molecular self-assembly, mixed phases of long and short chain alkyls have been prepared. As one of such possible combinations, C_3 chains have been mixed with C_{18}.[12]

Vapour-Phase Reactions

Modification of silica gel with volatile or gaseous compounds is performed in the vapour phase. Industrial-scale reactors and laboratory scale gas adsorption apparatus have been used. In the industrial field, fluidized bed and fluid mill reactors are of main importance.

For laboratory-scale modification, distinction has to be made between static and dynamic adsorption procedures. In a static procedure, the substrate is contacted with a known volume of gas at a well-defined pressure. The modifying gas may be stationary or circulating in a closed loop. Modification in a static gas adsorption apparatus allows the careful control of all reaction parameters. Temperature and pressure can be controlled and easily measured. Adsorption kinetics may be determined by following the pressure as a function of the reaction time.

In the dynamic gas modification procedure, the reacting gas is passed through the substrate and dissipated. Temperature and gas flow may be controlled, with the limitation of pressure build-up at the substrate site. Relatively large amounts of gas may be passed through the sample.

The main difference between the two procedures is the type of control of the reaction mechanism. For static reactions, the reaction velocity is controlled thermodynamically. In this case, the velocity is mainly controlled by the equilibrium constants for the reactions at a given pressure. In the dynamic regime, on the other hand, a more intimate contact between reagent and substrate occurs. Moreover, gaseous reaction products are captured constantly and the overall process is under kinetic control. Detailed experiments on the difference in kinetics between the two processes have been performed by Yongan.[13]

Hydrolysis and condensation behaviour are analogous to modification procedures in dry organic solvent. However, controlled gas phase procedures allow a better control of reaction conditions, leading to a more reproducible coating layer. While the possibility to form true monolayered coatings from solution has been doubted,[14,15] gas phase modification is generally agreed to give monolayer modification.

3. Modification of the Silica Surface with (Alkyl)Chlorosilanes

Strangely enough, a unified approach to the reactions of chlorosilanes with the silica surface is lacking in the international literature. This is probably due to the different reaction procedures that have been used and the different applications of the modified silica surfaces.

The high vapour pressure of the (methyl)chlorosilanes allows for a vapour-phase reaction. Moreover, these reactions are usually performed on amorphous silica with a high surface area, which is very suitable for a detailed study of the surface species by means of FTIR, XPS and NMR.

The higher order alkylchlorosilanes (C_8 and C_{18}) have historically been treated in the same way as organosilanes. The reaction inevitably occurs in the liquid phase and is usually followed by a curing step. The extremely low surface of the silicon wafers and the deposited SiO_2 layers used for self-assembled-monolayers does not

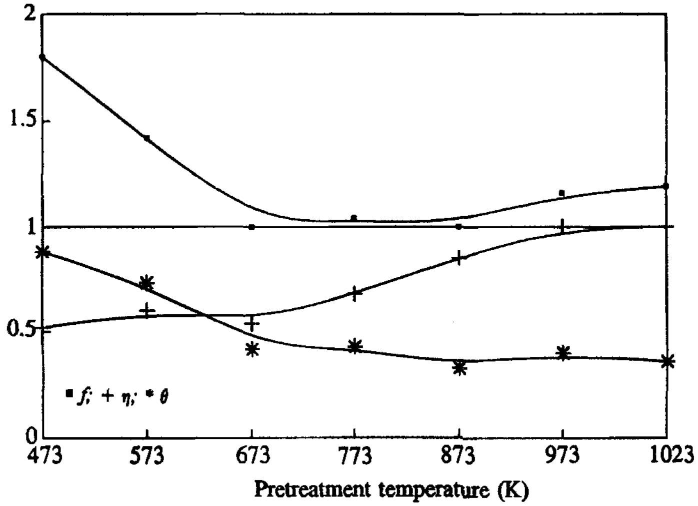


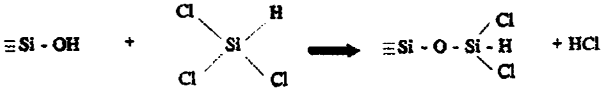
Figure 7. Effectiveness, surface coverage and stoichiometry factor for the reaction of silica gel with TCS. Reactions occured at 623 K for 1h.

allow a spectroscopic quantification of the surface species. A completely different type of analysis technique is used here mainly to determine the quality (roughness and uniformity), the adherence (parallel or at random) and the hydrophobicity of the coated layer. Often used techniques are AFM (Atomic Force Microscopy), ellipsometry and chromatography.

3.1. Vapour-Phase Reactions with (Methyl)Chlorosilanes

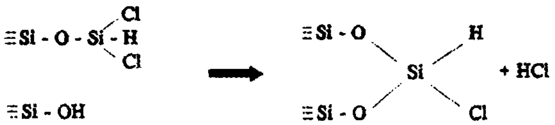
The reactions between (methyl)chlorosilanes and the surface of silica have been investigated by many researchers, primarily because of the utility of these reagents as coupling agents in polymer chemistry and as surface deactivating agents in chromatography.

Few studies are devoted to the reaction of silica with trichlorosilane (TCS). The earliest report, dealing specifically with the TCS modification of silica, is the one of Chuiko et al.[16] A silica, pretreated at 673 °K, was reacted with TCS vapour at room temperature. The authors observed a complete disappearance of the free hydroxyl groups, due to reaction (A).

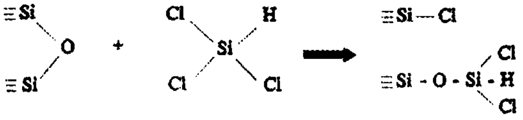

(A)

They claimed that, under these conditions, a bimolecular reaction with two silanols is not possible, due to steric reasons. The distance between 2 Cl groups in trichlorosilane is 0.33 nm, whereas the mean distance between 2 OH groups on a silica surface, annealed at 673 °K, is considerably larger.

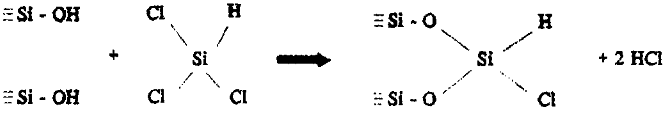
Low[17] refined Chuiko's findings in 1981. He confirmed the statement that bimolecular reactions are not likely to occur at high pretreatment temperatures, but he suggested a secondary, (consecutive) reaction (B):


(B)

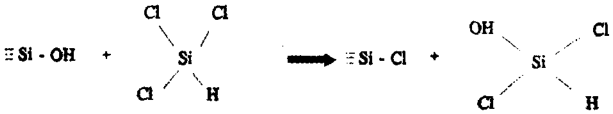
He also suggested a side reaction (C) with so-called *strained* siloxane bridges.


(C)

In the meantime, many articles were published on the reaction of methylchlorosilanes with silica. Especially the publications of Hair and co-workers[18-22] have gained widespread attention. Using infrared band integration of the hydroxyl region, and putting the normalized data into the integrated form of the rate equation, they found that all polyfunctional methylchlorosilanes followed a reaction order of 1.6 at a reaction temperature of 573 °K. This means that 60% of the silane reacts bifunctionally. The bimolecular reaction of trichlorosilane with silica is presented as reaction (D):


(D)

In addition to this reaction, they noticed a positive intercept in the fitting of the experimental data by the rate equation, and ascribed this effect to an initial fast reaction (E):



(E)

In his kinetic plots, Hair only considered a monomolecular reaction (A), and a bimolecular reaction (D). He never mentioned the secondary reaction (B) or the side reaction (C). Although his general conclusions on the stoichiometry of the reaction may be correct, it is not excluded that other reactions than the two he mentioned are involved.

Summarizing, the study of the chlorosilylation of the silica surface has given rise to five possible reaction mechanisms, that are believed to occur simultaneously or consecutively. In order to quantify all five mechanisms, the researcher needs at least five independently measurable and quantifyable parameters. However, there are often fewer independently measurable parameters than unknowns. In these cases, only semi-quantitative data can be obtained.

One possible way to optimize such a chemical modification, is to express the experimental data in terms of effectiveness, surface coverage and stoichiometry.

2.1.2. Effectiveness, Surface Coverage and Stoichiometry[23]

In the case of a chemical modification of silica, the ratio of the number of hydroxyl groups undergoing reaction ($n_{OH(r)}$) to the total number of initial hydroxyl groups ($n_{OH(t)}$) reflects the effectiveness factor η. If the specific surface area (S_{BET}) of the silica sample does not change during the reaction, the effectiveness factor can also be expressed as a ratio of the number of silanols per nm^2 (α_{OH}).

$$\eta = \frac{n_{OH_{(r)}}[\text{mmol/g}]}{n_{OH_{(t)}}[\text{mmol/g}]} = \frac{\alpha_{OH_{(r)}}\left[\#/\text{nm}^2\right]}{\alpha_{OH_{(t)}}\left[\#/\text{nm}^2\right]} \tag{1}$$

However, using η as the only parameter in the optimization can often be misleading, since the maximum degree of conversion is not only determined by the number of reacting hydroxyl groups, but also by the mean cross-sectional area (A_m)

of the reacted group (steric hindrance effects). The surface coverage (θ) is defined as the ratio of the actual bonded species on the surface to the maximum number of bonded species that is sterically possible.

$$\theta = \frac{\alpha_{exp}}{\alpha_{max}} = A_m \bullet \alpha_{exp} \qquad (2)$$

Effectiveness and surface coverage are only indices for the amount of silanols that have reacted. Depending on the functionality of the modifier, various reaction mechanisms can take place.

A third parameter has to be introduced, yielding information on the different kinds of surface species. A factor *f*, reflecting the stoichiometry of the reaction, can be defined as:

$$f = \frac{n_{OH_{(r)}}}{n_{modifier_{(r)}}} = \frac{\alpha_{OH_{(r)}}}{\alpha_{modifier_{(r)}}} \qquad (3)$$

For a monomolecular reaction, f is 1. For a completely bimolecular reaction, where 2 silanol molecules react with one molecule of modifier, f = 2.

Let us now apply these general formulae to the chemisorption of trichlorosilane on silica. Assuming that the reaction of trichlorosilane with silica gel only causes monodentate (reaction (A)) and bidentate (reactions (B) and (D)) species, the general formulae for effectiveness, surface coverage and stoichiometry can be rewritten in function of $OH_{(r)}$ (number of reacted silanols, quantified by FTIR spectroscopy[23-25] and Cl on the surface.

Since in the reaction (A), 1 silane linkage includes 2 Cl groups and for a bidentate species, 2 silane links include 1 Cl group, one can write:

$$\frac{Cl}{OH_{(r)}} = \frac{2MS + BS}{MS + 2BS} = \frac{2 - BS}{1 + BS} \qquad (4)$$

where BS stands for the percentage of bidentate species and MS for the percentage of monodentate species. The monodentate species can be substituted in Equation (4), following the initial assumption that MS + BS = 1.

Rewriting Equation (4) as a function of BS, one obtains:

$$BS = \frac{2 - \frac{Cl}{OH_{(r)}}}{1 + \frac{Cl}{OH_{(r)}}} \qquad (5)$$

Formula (3) for the stoichiometry factor can then be actualized for the TCS chemisorption as:

$$f = \frac{OH_{(r)}}{\left[(1 - BS)\bullet OH_{(r)}\right] + \left[BS \bullet \frac{OH_{(r)}}{2}\right]} \qquad (6)$$

When optimizing the surface modification, the first important factor to consider is the effectiveness. The pretreatment temperature of the silica, the reaction temperature and reaction time must be controlled to yield an effectiveness of 1. Remaining hydroxyl groups on the surface of silica gel are highly undesirable, since they would cause uncontrollable side-effects in the following reaction steps.

Of all conditions, yielding an O of 1, those must be chosen which produce the highest amount of reactive chlorine groups. This means that the surface coverage must be as high as possible, and that the stoichiometry must approach unity.

Figure 7 shows the three parameters as a function of the pretreatment temperature of the silica. All reactions occurred at 623 °K for 1 h. The surface coverage curve is decreasing as a function of pretreatment temperature. A maximal surface coverage is only possible at pretreatment temperatures below 673 °K. However, as can be inferred from the figure, this situation is never achieved. Therefore, it is recommendable to study the effectiveness curve. An effectiveness of 1, a very important condition to avoid unreacted silanol groups, only occurs at pretreatment temperatures of 973 °K or higher. Based on these two curves, a pretreatment temperature of 973 °K seems to be the best choice: it is the lowest temperature (highest amount of reactable silanols) at which complete silylation occurs.

The stoichiometry curve can be subdivided into three regions. In the temperature region between 473 °K and 673 °K, bimolecular and/or secondary reactions are sterically possible. The stoichiometry factor of 1.6, found by Hair[21] for the reaction of silica, pretreated at 573 °K, with methyltrichlorosilane, is reflected in

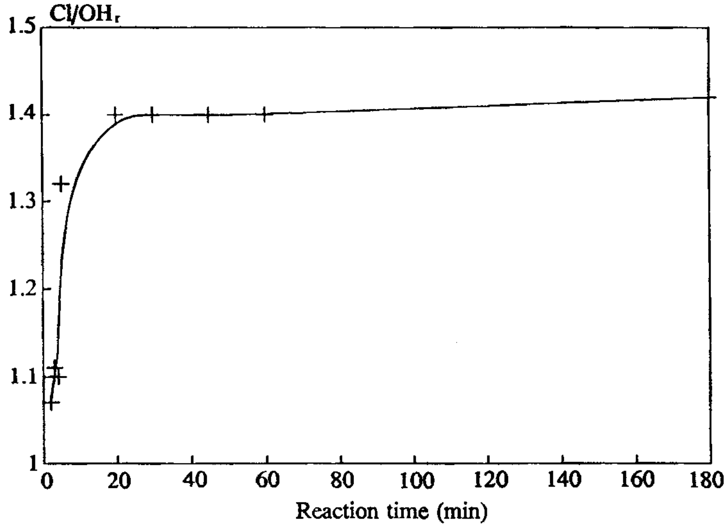


Figure 8. The ratio Cl over OH (reacted) for the reaction of Kieselgel 60 (pretreated at 973 K) with TCS (at 623 K) as a function of reaction time.

these experiments. Equation (6) proves to be a very useful formula for a relatively fast evaluation of the stoichiometry factor, provided that the initial condition (MS + BS = 1) is fulfilled. The question whether these secondary species originate from bimolecular or secondary reactions, cannot be solved by this curve. In the temperature region 673 °K-873 °K, the silanols are too far separated to be involved in secondary or bimolecular reactions. In this region the stoichiometry factor is obviously 1.

In the pretreatment region above 873 °K, the silanol loading on the surface is very low (*cfr.* Figure 1) and the formation,of bidentate species is excluded for steric reasons.[23] In this temperature region, f has no longer a physical meaning, since the condition MS+BS=1 is no longer fulfilled, and side reactions (C) and (E) have to be considered.

Figure 8 shows the ratio Cl/OH$_r$ for the reaction on Kieselgel 60 (pretreated at 973 °K) with TCS at 623 °K at different reaction times. During the first 5 minutes of the reaction, this ratio is close to 1, meaning that 1 OH is replaced by 1 Cl group. It seems very unlikely that this value is due to a combination of primary and secondary reactions.[23] Therefore, this value is most probably caused by the reaction (E). This reaction indeed yields a Cl/OH value of 1. So, Figure 8 confirms Hair's statement that reaction (E) should be considered as a *fast initial reaction*.

Reaction with Strained Siloxane Bridges

The above does not mean that reaction (C) with the siloxane bridges does not occur. On the contrary, it is possible to present a number of arguments that suggest a reaction with strained siloxane bridges at high pretreatment temperature of the silica. Not only the *concentration* of the siloxane bridges increases with rising pretreatment temperatures, they also show an enhanced *reactivity*. It is assumed that with higher degassing temperatures, the remaining isolated hydroxyls are progressively removed and that various types of structural changes must occur, giving rise to the so-called *strained* siloxane bridges, which exhibit an enhanced activity. Morrow[26] stated that site is assumed to be an unsymmetrical siloxane bridge, containing an electron deficient silicon atom, which can act as a Lewis acid centre.

A relatively easy way to check the existence of a reaction with strained siloxane bridges is to replace and/or block all surface hydroxyl groups by a reaction with hexamethyldisilazane. In this way, we were able to prove that reaction with strained siloxane bridges occurs at reaction temperatures > 623 °K and pretreatment temperatures > 973 °K.[23]

3.2 Liquid-Phase Reaction with Alkylchlorosilanes (C_8 - C_{18})

The formation of monolayers by self-assembly of organochlorosilanes on various surfaces[27-30] and organosulfur compounds on gold[31,32] is well established. The durability of the self-assembled monolayer is highly dependent on the effectiveness of the anchoring to the surface. On gold, the attachment to the surface is due to an interaction of sulphur end groups with the gold surface. However, the nature of the attachment of the organochlorosilane with the surface is ill-defined.[33-35]

Octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, henceforth denoted OTS) is the most common organosilane used for the formation of self-assembled monolayers and, when reacted with silica surface, finds extensive use as a bonded phase in liquid chromatography applications.[36] A common mechanism proposed for attachment of the chlorosilane to the surface[33,37] involves the hydrolysis of the chlorosilane groups with water which is already on the surface of the substrate.

The silanols which are formed then condense with the surface hydroxyls groups to form stable linkages to the substrate. In practice, a curing process is usually required to condense adjacent silanols attached to the organosilane to form a cross-linked 'mat' on the surface. Part of the difficulty in determining the nature of the attachment to the surface arises from the lack of direct spectral evidence, due to the low surface areas of the substrates.

In 1992 Tripp and Hair[38] unified the two chlorosilane approaches by reacting OTS with a high surface area amorphous silica gel, in order to probe spectroscopically the different surface species. Using a home-made *in situ* liquid infrared cell, they derived following conclusions:

> 1. OTS does not react with degassed silica at room temperature. The infrared band of the free hydroxyls shifts to 3690 cm^{-1} but does not change in intensity. This indicates that the chlorosilane is physisorbed (H-bridged) on the silica surface. Subsequent degassing removes all adsorbed species.
>
> This conclusion is not surprising. Also, (methyl)chlorosilanes do not react with the silica surface at room temperature. Reaction temperatures > 473 °K are required to achieve noticeable reaction. The boiling point of octadecyltrichlorosilane is 433 °K. It would be very interesting to see what happens at reflux temperature.
>
> 2. OTS does react slightly with 'wet' silica at room temperature, containing multilayers of water on the surface. The broad band at 3650 cm^{-1} decreases slightly, and a band at 3350 cm^{-1} arises, attributed to trisilanols.[39,40] Tripp and Hair[38] state that the first layer of water is strongly bonded to the surface and does not participate in the hydrolysis of the chlorosilane headgroup of the OTS molecule.
>
> Subsequent layers would be less strongly bonded to the surface and would be able to participate in direct hydrolysis of the OTS.

Since the hydrolysis and adsorption of the OTS occurs with the subsequent layers of water, an optimum level is necessary to form robust films: too little water results in the formation of an incomplete monolayer, whereas a thick water layer causes a polymerization of the OTS with the water, resulting in a very poor adherence to the silica surface.

Not only octadecyltrichlorosilane is unreactive towards dry silica at room temperature. This is also the case for the chlorosilanes and the methylchlorosilanes. It was stated earlier that the vapour phase reaction occurs at elevated temperatures (> 473 °K). This high-temperature constraint limits potential gas phase silanizing agents to those which have a high thermal stability and sufficient vapour pressure.

In practice, the common method for silanization of silica is to mix a chlorosilane with a hydrated silica in a suitable organic solvent. A common mechanism reported for this reaction is that the chlorosilane is first hydrolyzed by the water and this is followed by the condensation with the surface hydroxyl groups to form a strong Si-O-Si surface bond.[37]

If the starting silane contains a trichlorosilyl headgroup, then further condensation between adjacent silanes can occur, yielding a two-dimensional polysiloxane network. The occurrence of the first step, the hydrolysis of the chlorosilane to a silanol by the surface water is amply supported by the literature.[33,34,38,41]

At either the solid/gas or solid/liquid interface the chlorosilane does not adsorb onto a completely dehydrated silica and is hydrolyzed to the silanol with the surface water of a hydrated silica.

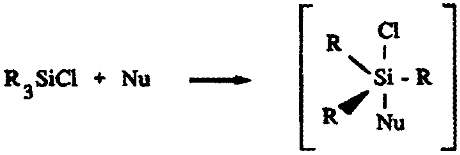
However, Tripp and Hair[42] have shown that the second critical step (i.e. condensation of the silanol with the surface hydroxyls groups) does <u>not</u> occur. At the solid/gas interface, the silanol adsorbs on the surface but does <u>not</u> undergo condensation or polymerization, whereas at the solid/liquid interface, the silanol polymerizes in solution and adsorbs on the surface.

In neither case there is a strong Si_s-O-Si bond formed with the substrate. It is the absence of Si_s-O-Si surface linkages that is responsible for the general lack of robustness of silanized surfaces prepared from solution.

In a subsequent publication, Tripp and Hair[43] describe a new method to chemically bind chlorosilanes to the surface under mild reaction conditions. In fact, there are two possible ways for a base-catalyzed chemisorption of chlorosilanes on silica.

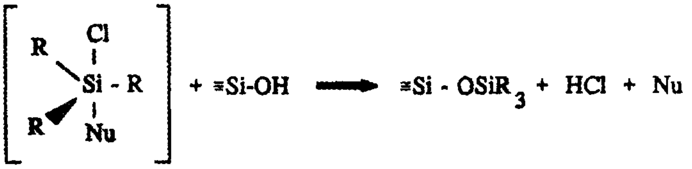
One possible strategy is to use a base to promote the reaction of chlorosilanes with the surface silanols.

In essence, this reaction proceeds by a one-stage nucleophilic mechanism through the formation of a pentacoordinate silicon intermediate (reaction (F)).



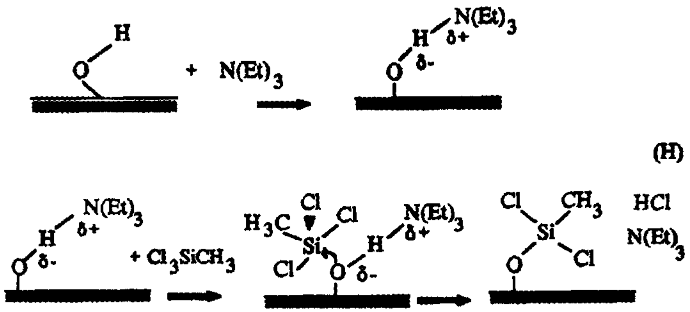
(F)

The Si-Cl bond is lengthened in the intermediate and is susceptible to attack by a second nucleophile:[44]



(G)

An alternative mechanism for the base-promoted reaction of silanes with silica has been described by Blitz et al.[45] In this mechanism, the base attacks directly to the surface silanols. The bonded amine renders the silanol more nucleophilic which then attacks the silicon atom of an approaching silane, giving rise to a pentacoordinate intermediate.



(H)

In both mechanisms a pentacoordinate intermediate is postulated. The main difference is that the pentacoordinate intermediate is formed by attachment of the amine to the chlorosilane in one case and by attachment to a surface Si-O group in the other. The main problem associated with base-catalized silanization is that it is very difficult to prevent polymerization of the silane in solution. Rapid polymerization of the chlorosilane occurs in solution unless extreme precautions are taken to exclude contact with residual water.

Thus, in a typical base-promoted silanization on silica, it is more likely that both polymerization and surface reaction occur to some extent. Both mechanisms can account for polymerization. The intermediate formed by attachment of the amine to the chlorosilane could react with nucleophiles (i.e., molecular water) other than the surface silanols. In the mechanism described by Blitz et al., the chlorosilane (either attached or in solution) could be hydrolyzed to the trisilanol by molecular water and the trisilanol offers an additional source of silanols for base attachment and subsequent polymerization. Polymerization often results in a thick silane layer on the surface that, in many cases, is undesirable.

Polymerization is not possible in the complete absence of water or when reactions are carried out using monochlorosilanes. However, trichlorosilanes are attractive because it is possible to increase the strength of the adsorbed silane layer through cross-linking between adjacent molecules. The other approach, the exclusion of trace quantities of water, especially in solution, is extremely difficult and costly.

In 1993, Tripp and Hair[43] described a method to promote the direct reaction of the chlorosilyl headgroup with the surface hydroxyls groups, using a nitrogen-containing base (triethylamine). In this method, polymerization is avoided because the base and chlorosilane are not added simultaneously but subsequentially in a two-step process.

4. Modification of the silica surface with Aminosilanes

For a fundamental understanding of the processes occurring during the modification, a distinction has to be made between processes taking place in the reaction step and in the post-reaction curing.

In the reaction phase, three types of interaction of the aminosilane molecule (in this case APTS, γ-aminopropyltriethoxysilane; $(CH_3CH_2O)_3Si\text{-}CH_2CH_2CH_2NH_2$) with the silica surface have been reported[46,47] (Figure 9). The amine may enter into a hydrogen bonding interaction with a surface hydroxyl group. The basic amine may abstract a proton from a silanol group and form an ionic bond. This type of interaction is much more stable than the first one. The hydrogen-bonded molecules may self-catalyze the condensation of the silicon side of the silane molecule. Thus, a covalent siloxane bond is formed.

In order to determine the extent of all three of the interaction types in the reaction phase, a leaching test was performed on a non-cured sample.[48,49] Upon stirring in ethanol, the weakly bonded silane molecules desorb and the amount is

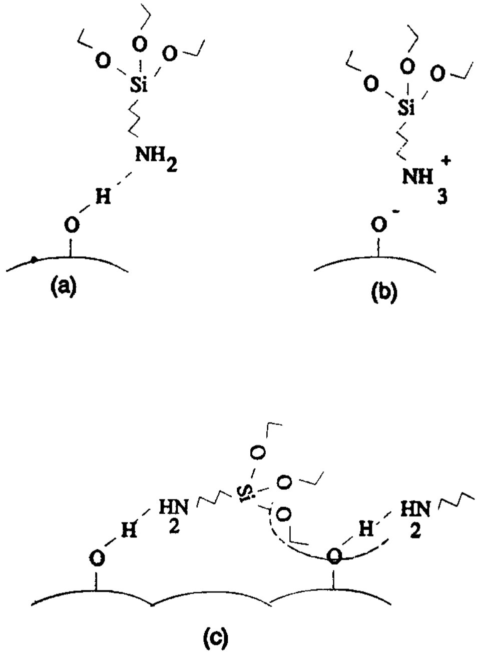


Figure 9. Surface - aminosilane interactions in the loading step, (a) hydrogen bonding, (b) proton transfer, (c) condensation to siloxane.

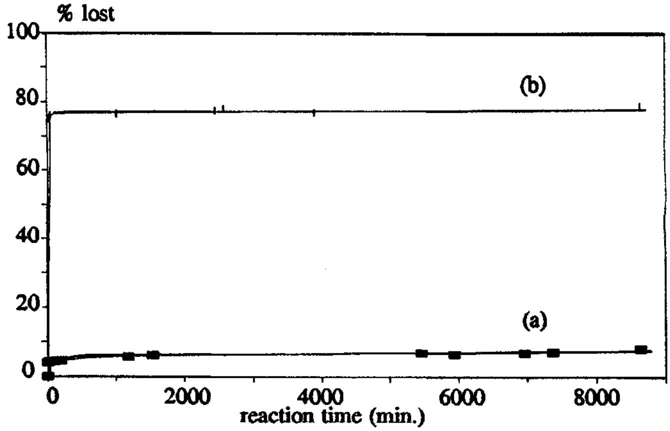


Figure 10. Ethanol leaching curves of uncured modified silica; (a) APTS, (b) n-butylamine.

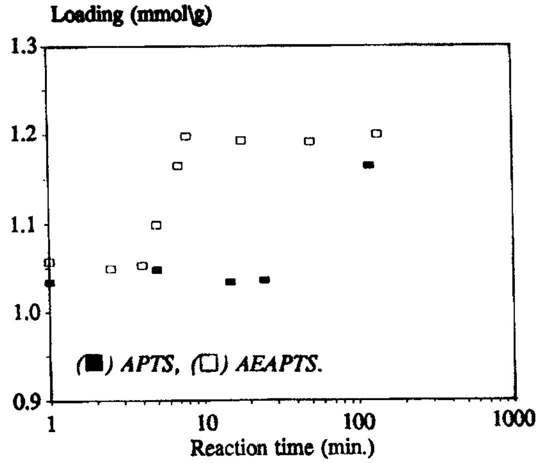


Figure 11. Silane loading on dried mesoporous silica gel as a function of reaction time.

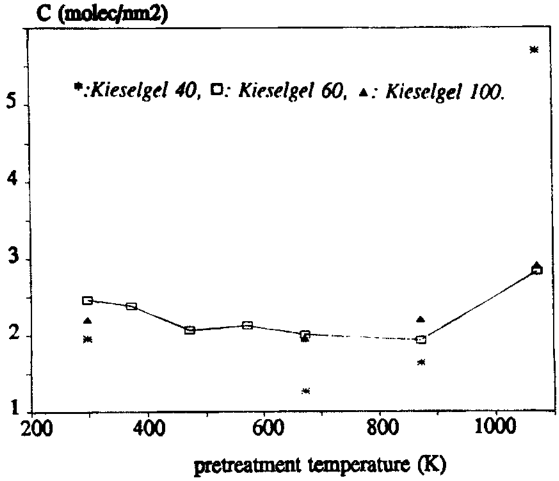


Figure 12. Total surface coverage of APTS modified silica gel, with variable pretreatment temperature.

measured quantitatively by means of a colour reaction with salicylic aldehyde.[50] Physisorbed molecules desorb, while ionic and covalently bound molecules are stable towards this ethanol leaching. In Figure 10, the relative percentages of silane lost from the surface is displayed as a function of leaching time.

From the APTS leaching curve (curve **a**), we obtain a relative amount of about 10% of the coating which is only physically bonded to the surface before curing.

In order to distinguish the ionic bonding from the covalent attachment, the same test was performed using n-butylamine (curve **b**). The amine group interaction of butylamine is similar to APTS, but there is no silicon atom present to form covalent linkages. 22% of the butylamine appears to be stable towards the ethanol leaching. Therefore, it was concluded that 22% of the coating is in ionic interaction with the surface, 10% is hydrogen bonded and 68% is covalently bonded after 2h of reaction at room temperature.

The course of the aminosilane deposition during the reaction phase was measured using free sampling analysis. After certain reaction times, samples are taken from the reaction mixture, which are then frozen to stop the reaction. After melting and separation, the amount of reacted silane is measured.

The reaction profiles of APTS and AEAPTS (N-β-aminoethyl-γ-aminopropyltrimethoxysilane; $(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$) are displayed in Figure 11. Both compounds reach an equilibrium adsorption within 1 min of reaction. This reflects the quick adsorption of the amine group, forming hydrogen bonds with the surface silanol groups.

For the AEAPTS, carrying two amine groups, a two-step adsorption is found. This indicates that an amine group of the organic chain remains free in the first step and is able to adsorb an additional layer of silane molecules. Since secondary amines are better acceptors for hydrogen bonds, it will be the primary amine function at the end of the organic chain that remains free. Upon adsorption of the secondary layer, an equilibrium situation is again reached.

For the monofunctional silane, the first equilibrium is followed by an additional adsorption, which does not have a step-wise profile. The equilibrium situation is related to the localized adsorption of silane molecules on the surface hydroxyl groups, thus forming a monolayer coating on the surface.

In order to study the effect of substrate related parameters, the pretreatment temperature of the silica substrate may be varied. In Figure 12, the total coverage, expressed as number of APTS molecules per nm^2, is displayed as a function of the pretreatment temperature.

The total coverage is a measure for both chemically and physically adsorbed silane species. The degree of surface hydration and hydroxylation, as well as the specific surface of the silica, varies with varying pretreatment temperature. In the low temperature region (< 473 °K) a decrease of surface loading with increasing temperature is observed. If surface water is present, surface adsorbed molecules hydrolyze and condense with other silane molecules. Thus, a multilayer coating is obtained.

At higher pretreatment temperatures, a constant loading is observed. While the degree of hydroxylation decreases in this temperature region, the specific surface area remains constant. Therefore, the total coverage is controlled by the specific surface area of the silica, rather than by the hydroxyl group content. Silane molecules are deposited on the silica surface with each molecule covering 0.5 nm^2. The previously mentioned course of APTS deposition, may be interpreted as a silanol group specific initial deposition, reaching equilibrium, followed by a filling of the free space on the silica surface. Non-specifically adsorbed molecules will desorb quickly in the curing phase.

For silica pretreated at 1073 °K, an increased surface coverage is observed. This may be due either to the structure of the coating layer, involving multilayer formation or to a change in the molecular orientation at the surface, or to the different porous structure of the 1073 °K pretreated silica. None of these hypotheses can be excluded on the basis of these data. The participation of strained siloxane groups[51] is another possible explanation. It has been previously reported that those siloxanes may enter into physical and chemical interactions with silanes[52,53] and ammonia.[54,55] Here it appears that aminosilanes are also able to react with strained siloxane bridges.[56] It has been generally accepted that the majority of the silane-to-surface siloxane bonds are formed in the curing phase. Above, we have demonstrated that already in the reaction phase 68% of the APTS molecules have formed at least one chemical bond with the surface. The formation of covalent bonds in the curing phase has been probed by a similar ethanol leaching test.

In Figure 13 the stability towards ethanol leaching is plotted as a function of curing time. Curves for both APTS and APDMS (γ-aminopropyldiethoxymethylsilane; $(CH_3CH_2O)_2CH_3SICH_2CH_2CH_2NH_2$) are displayed. It can be seen that the APTS reaches its maximal stability within 3h of curing. Only 2% of the coating remains merely physisorbed. For the APDMS, maximal stability is reached after a much longer time. APDMS needs 20h of curing before maximal stability is reached. The difference in condensation behaviour is clearly due to the different number of ethoxy groups in the silane molecule. The higher number of ethoxy groups of the APTS molecule causes a much faster stabilization.

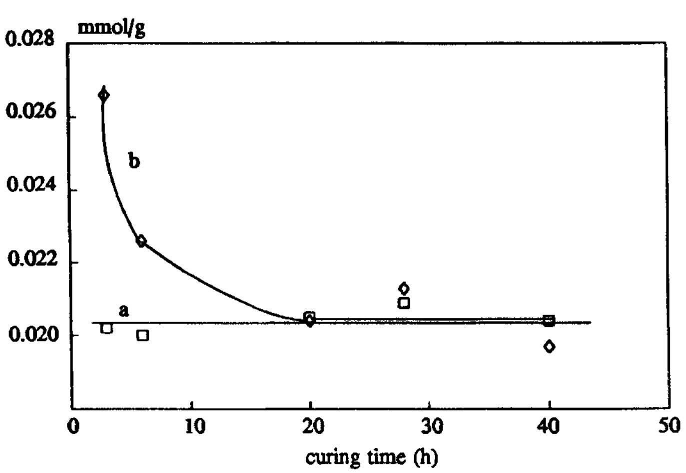


Figure 13. Amount of physisorbed silane molecules per g of modified silica as a function of curing time in vacuum.

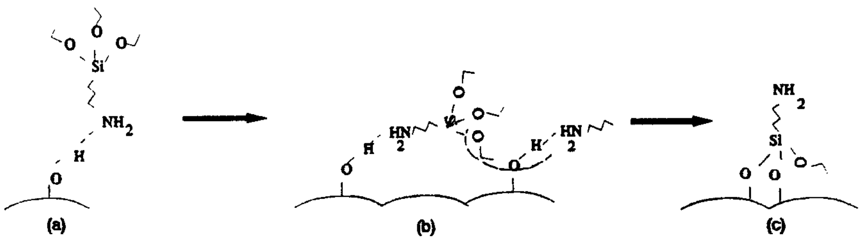


Figure 14. Flip mechanism for APTS reaction in dry conditions, (a) physisorption, (b) condensation, (c) main structure after curing.

Concerning the amine side of the molecule, valuable information can be drawn from ^{13}C solid state NMR spectra. The results have been reported elsewhere,[56] but it is worthwhile to recapitulate the conclusions. From the position of the peak due to the β-C atom of the propyl chain, information on the mobility of the aminopropyl chain may be obtained. It appeared that upon curing, the amine group relinquishes its interaction with the silica surface.

Therefore, the aminosilane molecule turns from the original amine-down position in the reaction phase towards an amine-up position after condensation. This is called the flip-mechanism (Figure 14).

SUMMARY

In this review, we have discussed the silylation of silica with various silanes, including chlorosilanes, organosilanes and aminosilanes, both in the liquid phase and in the gas phase. In every case, the reaction mechanism involved is more complex than is often believed. Many reactions can occur simultaneously and the resulting surface layer depends largely on the synthesis conditions.

Special attention should be given to the role of water in the synthesis procedure. Water can occur as physisorbed molecules on the substrate prior to modification, but it may be involved in the reaction mixture itself or even as humidity during the post-reaction curing step. In every case, the water molecules have an enormous impact on the modification reactions, causing a polymerization of the silane molecules, resulting in a thick but irreproducible and irregular surface layer.

Since in these modification reactions, there are often more unknowns than independently measurable values, the parameters that facilitate the optimization of a modification, such as effectiveness, surface coverage and stoichiometry, have been introduced and exemplified.

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