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Use of *p*-Toluenesulfonic Acid for the Controlled Grafting of Alkoxysilanes onto Silanol Containing Surfaces: Preparation of Tunable Hydrophilic, Hydrophobic, and Super-Hydrophobic Silica

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Abstract: The modification of Aerosil 200 has been carried out using methoxysilanes in toluene reflux, with *p*-toluenesulfonic acid as the catalyst. Both trimethoxyalkyl silanes (methyl, ethyl, propyl, butyl, hexyl, octyl, and octadecyl) and trialkylmethoxy silanes (trimethyl and dimethyloctyl) have been used. The surface has been studied by ^{29}Si NMR, ^{13}C NMR, elemental analysis, thermogravimetry, water contact angle, and BET analysis. When incorporating trimethoxysilanes, a plateau of modification was achieved after 1 h of reflux, while when using trialkylmethoxy silanes, a longer time of about 7 h was required. The average number of molecules incorporated in both cases has been well above those reported by other authors in similar reactions and in much shorter times. Depending on the modification agent and on the experimental conditions, the resulting organosilicas are in seven cases superhydrophobic, in three cases hydrophobic, and in two cases hydrophilic. Two structural origins for superhydrophobicity have been identified in these samples: almost complete disappearance of water accessible surface silanols (smallest methoxysilanes) and shielding of would-be water accessible surface silanols by long aliphatic tails. These features can be very precisely controlled.

1. Introduction

The modification of silica surfaces via the reaction of surface silanols with organic molecules has long been studied, and the so-prepared organosilicas have found applications in many fields of chemistry, for instance, in chromatography[1−7] and catalysis.[8,9] More recently, they appear as a key topic in areas such as polymer nanocompounds[10−13] and the development of hydrophobic and superhydrophobic materials.[14]

The use of monofunctional silanes enables the unequivocal calculation of the number of silane molecules bonded to the surface by means of the carbon content in the substrate.[1] On the other hand, the chemistry involved in the reaction of silica surface silanols with trifunctional aminosilanes, alkoxysilanes, or halosilanes is quite simple to produce but very difficult to characterize, a feature shared by almost all chemistry derived from the reactivity of multifunctional molecules. This is so because the number of different products of reactions involving trifunctional molecules is, except in specific cases, enormous.[1−6,15,16] In the 1970s, pioneer work by Lippmaa and co-workers[17] initiated the elucidation of ^{29}Si NMR Si−O−Si signals. Since then, the use of ^{29}Si NMR has greatly helped in the characterization of the silicon containing structures.[18−24]

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Table 1. Summary of Reaction Conditions Employed in Organic Modification of Aerosil 200

sample type	PTSA	reflux time (h)	reagents
A-TMS	yes	2	methyl (M), ethyl (E), propyl (P), butyl (B), hexyl (H), octyl (O), octadecyl (OD)
TA-MS	yes	2/7	octyldimethyl (OdM), trimethyl (TM)
V-TMS	yes	2	vinyl
O-TMS-w (octyl-TMS without PTSA)	no	2	octyl-TMS
OdM-MS-w (octyldimethyl-MS without PTSA)	no	2	octyldimethyl-MS

The most frequently used reaction conditions for silica modification with alkoxysilanes can be divided into two groups: the group of the anhydrous conditions, with no catalysis employed, very long reaction times, and very low incorporation of alkoxysilanes[22,25,26] and the group of aqueous conditions, acid catalysis (almost always HCl), low reaction times, and higher incorporation of alkoxysilane.[15,28,29] The former reaction condition leads to grafting, while the second leads to coating. Brunel et al.[27] showed recently that under anhydrous conditions, only the hydrophobic parts of the surface silica are able to react with the coupling agent. Majors and Hopper[28] found more than 30 years ago that the presence of surface adsorbed water increases the achievable levels of silane loading in the reaction. The effect of a surface water layer on the extent and nature of the hydrolysis−condensation reaction have also been studied.[27,29] Under the experimental conditions employed, the alkoxysilanes did not graft onto the surface. Some authors[30] believe, based on DFT calculations, that the presence of water pre-organizes the alkoxysilane molecule by dimerization and is thus necessary to build homogeneous monolayers on the silica. Finally, supercritical conditions have been used, and it has been reported that under these conditions, otherwise inaccessible hydroxyls are able to react with silanes.[31] The final properties of the organosilica depend on the type of reaction employed, as the final structure is not the same. In this connection, much effort is being devoted to the control and understanding of hydrophobicity/hydrophilicity and the chemical and morphological origins of superhydrophobicity.[32−37] In this work, results on the organic modification of a well-known silica (Aerosil 200) with a series of mono- and trifunctional alkoxysilanes will be shown. The use of a strong organic acid as a catalyst (*p*-toluenesulfonic acid), together with the reaction conditions employed, yields an organosilica with specific features. Quantitative characterization of the surface after grafting monomethoxy and trimethoxyalkyl silanes of increasing alkyl side chains is presented, together with a water contact angle study of all the organosilicas. All of them result to be hydrophobic or superhydrophobic, being that this behavior is explained by the nature of the surface coverage.

2. Experimental Procedures

2.1. Materials. The silica substrate, Aerosil 200 (Degussa), was not dried before derivatization reactions. The alkoxysilanes, methyltrimethoxy (Aldrich, 98%), ethyltrimethoxy (Fluka, 97%), propyltrimethoxy (Aldrich, 98%), butyltrimethoxy (ABCR, 97%), hexyltrimethoxy (Lancaster, 97%), octyltrimethoxy (Lancaster, 90%), octadecyltrimethoxy (ABCR, 95%), vinyltrimethoxy (Aldrich, 97%), trimethylmethoxy (Aldrich, 99%), and dimethyloctylmethoxy (Aldrich, 98%) were used without previous purification. The *p*-toluensulfonic acid (Aldrich, 98.5%) (PTSA) was also used as received.

2.2. Sylilation Reactions. Three grams of Aerosil 200 and 200 mL of toluene were placed in a three-necked flask equipped with a mechanical stirrer and a Dean−Stark reflux condenser. The mixture was stirred at 50 °C for 2 h to achieve a homogeneous dispersion, after which 0.02 g of PTSA and 0.06 mol of the alkoxysilane were added. No acid was added in the reactions without catalysis. The mixture was heated up to reflux temperature and continued to stir at this temperature for 2 h, after which it was checked that no further modification was produced (7 h for monomethoxysilanes). After cooling, the derivatized silica products were isolated from the reaction medium by centrifugation and purified by means of repetitive washing in ethanol (3 times) and further centrifugation. Finally, the reagent-free materials were dried at 100 °C for 12 h, prior to analysis.

The alkoxysilanes used and the experimental conditions for the reactions are listed in Table 1. The resulting organosilicas are named according to the assigned nomenclature in this table. For example, Aerosil 200 modified with propyltrimethoxysilane using acid catalysis is called hereafter P−TMS organosilica.

2.3. Surface Characterization. 2.3.1. Thermogravimetric Analysis. The TGA measurements were undertaken in a TA Q-500 apparatus at a heating rate of 10 °C min^{-1} and a nitrogen flow of 60 mL min^{-1}.

2.3.2. Microanalysis. Carbon content in the derivatized products was obtained by a LECO CHNS-932 apparatus. The error of this technique was ±0.3%.

2.3.3. ^{29}Si and ^{13}C CP/MAS NMR Measurements. ^{13}C and ^{29}Si NMR experiments were performed in a Bruker Avance 400 spectrometer (Bruker Analytik GmbH Karlsrube, Germany) equipped with a Bruker Ultrashield 9.4 T (^{13}C and ^{29}Si frequencies of 100.62 and 79.49 MHz, respectively), 8.9 cm vertical-bore superconducting magnet. In both cases, CP-MAS NMR spectra were acquired at ambient temperature by using a standard Bruker broad-band MAS probe. Representative samples were ground and packed in 4 mm zirconia rotors, sealed with Kel-F caps, and spun at 5 kHz. The 90° pulse width was 3.5−4.5 μs, and in all cases, high power proton decoupling was used. All free induction decays were subjected to standard Fourier transformation and phasing. The chemical shifts were externally referenced to TMS.

The ^{29}Si CP/MAS NMR spectra were obtained with 4 ms CP contact time, 4 s recycle delay, 41 000 averages, and 80 Hz line broadening.

The ^{13}C CP/MAS NMR spectra were acquired with 1 ms cross polarization (CP) contact time and a 3 s recycle decay. Each spectrum was obtained with 4608 averages and 200 Hz line broadening.

2.3.4. BET Surface. Nitrogen adsoption−desorption isotherms at 77 K of the Aerosil 200 and some organosilicas were measured with a Micromeritics TRISTAR 3000 instrument. Previously, the samples were outgassed at 300 °C under a nitrogen stream. Surface areas were calculated by applying the Brunauer−Emmet−Teller (BET) equation. Aerosil 200 shows a type II N_2 adsorption isotherm, implying a nonporous or macroporous structure.

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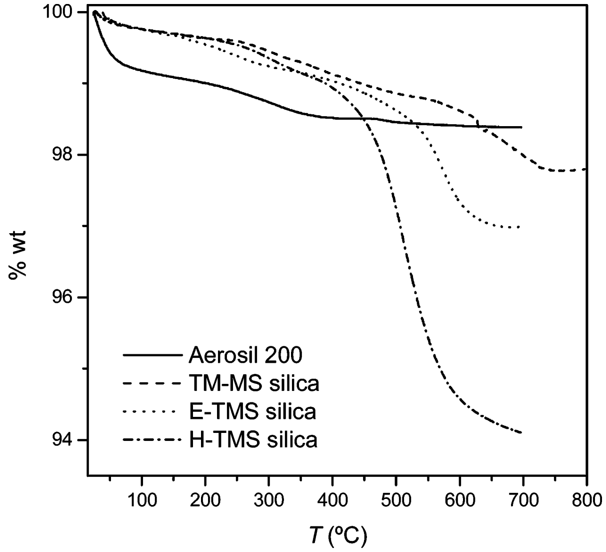


Figure 1. Weight loss in N_2 under dynamic conditions for Aerosil 200 and some selected derivatized products.

2.3.5. Water Contact Angle. An advancing contact angle was measured at 25 °C in a CAM 200 KSV apparatus by the drop shape method. Pictures of the drops have been taken every 0.01 s for the first second and every 5 s for 2 min afterward. Contact angles were obtained by placing the tip of the syringe near the sample surface and depressing the syringe to produce a constant drop volume. A Young−Laplace fitting method was used to determine the contact angle. Measurements were repeated on several probes for each sample, and the contact angle average value was used.

3. Results and Discussion

The organosilicas prepared in this work have been synthesized using the following conditions: a strong organic acid, soluble in water and toluene, has been employed (PTSA), silica has not been thoroughly dried, and a water layer on its surface is expected to exist. An anhydrous toluene reflux has been employed. The result is a much higher incorporation of alkoxysilane to the silica and much shorter times to reach a conversion plateau than when using toluene reflux and no acid catalysis. Grafting onto the surface silanols does occur, although the structure of the organic layer is not at all straightforward. In the next sections, quantitative or semiquantitative characterization of the structure has been accomplished.

3.1. Thermal Stability of the Organic Coverage: Thermogravimetric Analysis. Thermogravimetric analysis has been used to evaluate the decomposition temperature of the organic coverage. In Figure 1, the thermogravimetric curves of some selected samples are shown. The onset of thermal degradation is very similar for the alkyl-TMS series and vinyl-TMS and somewhat higher for the alkyl-MS series. The initial temperature is always at or over 330 °C, typical of alkyl chains.

A rough estimation of the mass incorporated to the silica can be made by TGA, although many circumstances contribute to this estimation being misleading, among them the condensation of silica surface silanols, detected above 200 °C in the thermogravimetric curve of Aerosil 200 included in Figure 1; more precise information can be obtained by elemental analysis of carbon wt %.

3.2. Estimation of the Reactive Amount Incorporated to the Silica: Microanalysis. Figure 2 shows the wt % of carbon incorporated to the particle as measured by microanalysis, for the alkyl-TMS series and the trialkyl-MS series, as a function of the alkyl side chain length.

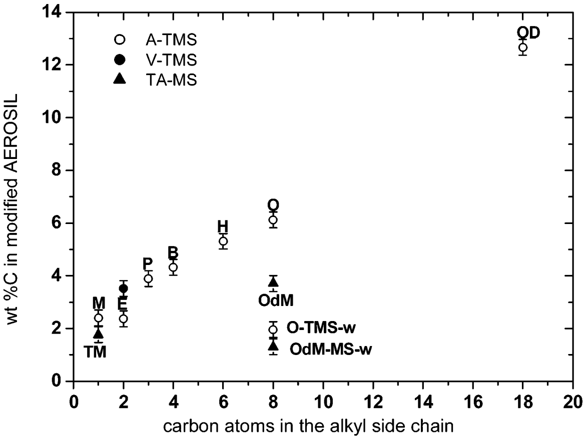
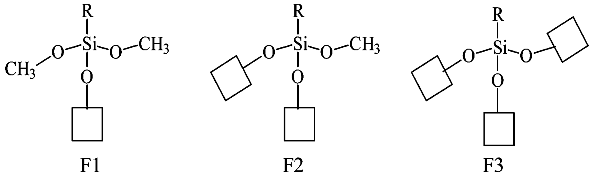


Figure 2. Wt % C in organically modified Aerosil 200 for all reactions, with and without PTSA, as a function of the methoxysilane alkyl chain length.

Chart 1. Species Bonded to Silica Surface According to Their Functionality[a]



[a] Functionality one (F1), two (F2), and three (F3). Squares stand for either a graft to the silica surface, a condensation with another methoxysilane molecule, or a hydrogen atom.

The calculations of the number of silane molecules per nanometer squared or of moles per gram of Aerosil from the raw data supplied by the elemental analysis are not at all simple for the TMS reagents. An unknown ratio of trialkoxysilanes with a functionality of 1, 2, or 3, depending on the extent of hydrolysis, are involved in the final product, giving rise to chains of silanes of unknown length and unknown distribution of side groups. Chart 1 shows the three functionalities. In the place of the unknown function, three different possibilities exist: a hydroxyl group, a graft to the silica, or condensation to another silane molecule. Some structures can be excluded: an obvious condition is that the species must be chemically joined to the surface, directly via a graft or indirectly via the condensation to silane molecules or chains of molecules that are on their turn grafted to the surface. All structures not fulfilling this condition were not considered. As for species chemically joined to the surface, only silane molecules attached thrice to the silica particle[1] can be excluded. To calculate either number of molecules per nanometer squared or of moles per gram from the carbon weight percentage, first a molecular weight of the molecule or molecular entity attached to the silica surface has to be supposed.[1,2] It is easy to see that the highest molecular weight of any of the A-TMS reagents is that corresponding to a molecule of functionality F1.

Obviously, the higher the molecular weight of the alkyl side chain, the lesser the importance of these variations. This divergence in the number of moles or molecules calculated under one or another assumption is shown in Figure 3 for the A-TMS

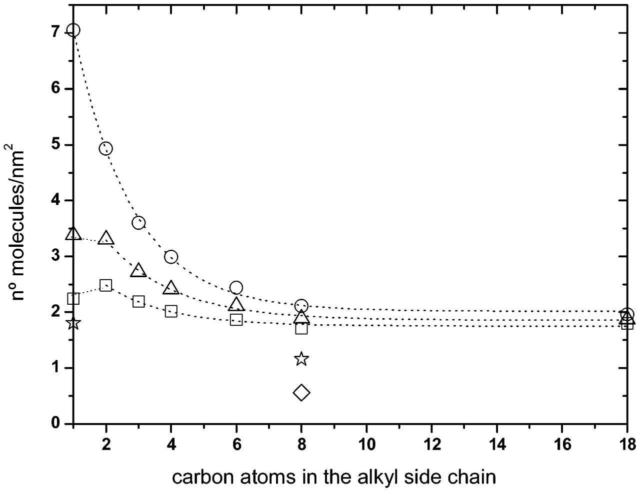


Figure 3. Number of molecules per nm^2 assuming functionalities 1 (□), 2 (△), and 3 (○), as obtained from the wt % C given by elemental analysis vs the carbon atoms in the methoxysilane alkyl side chain. The monoalkoxy organosilicas (☆) and uncatalyzed O-TMS-w organosilica (◇) also appear in the graph.

series. The number of molecules has been calculated according to ref 1 and 2 and taking into account the considerations made previously.

For octyl-TMS and octadecyl-TMS, being that their alkyl side chains are long, no great mistake is made if a number close to 2 molecules per nanometer squared is proposed. The limitations of microanalysis on itself to estimate the surface coverage are evidenced quite clearly in Figure 3. In a forthcoming section, efforts to reduce the uncertainty in the number of molecules are made by making use of NMR data. However, the progressive decrease in the number of silane molecules per nanometer squared as the alkyl side chain length increases is quite evident even at this stage. Figure 3 also shows that steric hindrance in the incorporation of new molecules to the surface exists, as is evidenced especially on increasing the side group size from methyl to butyl. Steric hindrance also exists in the monoalkoxy reagents, although it manifests itself more gently.

In addition, Figures 2 and 3 show the remarkable effect of PTSA on the reaction. The reaction yield increases by three both when the reagent is a monoalkoxy (octyldimethylmethoxy silane) or a trialkoxy (octyltrimethoxy silane). The most likely explanation is that the hydrolysis of the sole (octyldimethylmethoxy silane) or first (octyltrimethoxy silane) methoxy group is enhanced by the use of PTSA.[38] If hydrolysis is being enhanced, then not only the amount of alkoxysilane incorporated but also the structure of the species grafted onto the surface must change, as the ratio of F3 molecules will increase. This will modify the ^{29}Si NMR spectrum of the resulting organosilica.

3.3. ^{29}Si CP/MAS NMR. The ^{29}Si cross polarization (CP) MAS NMR technique, which enhances the sensibility of the silicon atoms near to protons, enables a thorough characterization of the surface species bonded to the silica. NMR cross polarization has been used to study the chemical structure of the silica surface. Figures 4 and 5 show the ^{29}Si CP/MAS NMR spectra of some organosilicas. Figure 4 shows the ^{29}Si spectra, and Figure 5 shows a magnification of the normalized Q region.

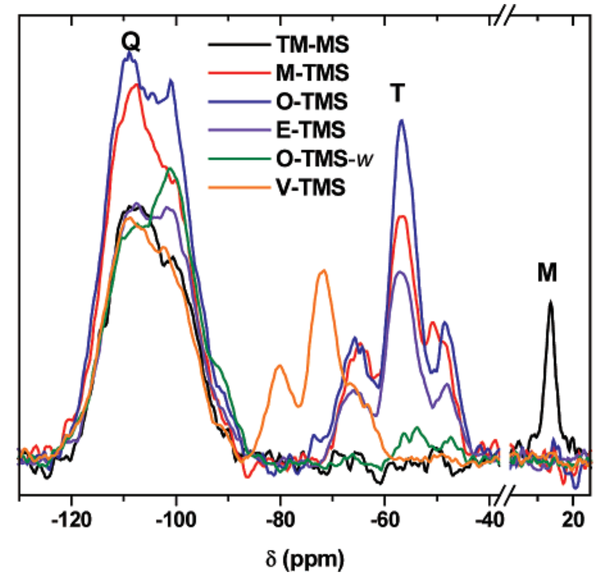


Figure 4. ^{29}Si CP/MAS NMR spectra for M-TMS, E-TMS, O-TMS, TM-MS, O-TMS-w and V-TMS modified silica.

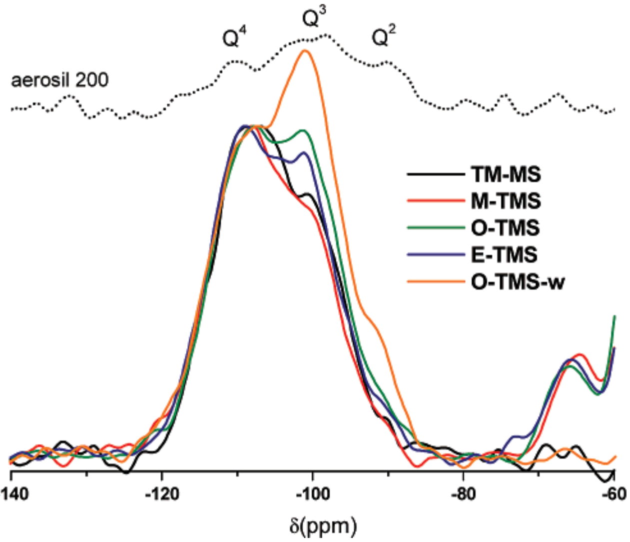


Figure 5. ^{29}Si CP/MAS NMR normalized Q region for M-TMS, E-TMS, O-TMS, TM-MS, and O-TMS-w modified silica. Unnormalized raw Aerosil 200 spectrum is included for comparison.

The monofunctional silane grafts onto the silica and gives rise to a signal at about 13 ppm, called the M signal, while the trifunctional silanes give rise to signals in the range of -80 to -50 ppm, called T signals. The comparison of the relative intensity of Q^4, Q^3, and Q^2 (assigned to siloxane groups at $\delta = -111$ ppm, free silanols at $\delta = -100$, and geminal silanols at $\delta = -90$ ppm, respectively)[17,18] in raw Aerosil 200 and in the four organosilicas indicates that methyl-TMS and trimethyl-MS employing PTSA modify the surface silanols to a much greater extent. The next in efficiency is ethyl-TMS, followed by octyl-TMS, and the less efficient modification is that of octyl-TMS without acid catalysis. This last one shows a clear Q^2 shoulder, which can only be suspected in the rest.

The information contained in Figures 3 and 5 strongly suggests that alkoxysilane units are not pre-condensed in the reaction medium when initially grafting onto the surface silanols and that condensation builds up after a first silane unit has grafted onto the surface: the fact is that there is a strong steric hindrance caused by the alkyl side chain length (depicted in Figure 3), but M−TMS and TM−MS react with roughly the

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Table 2. Percentages of T^1, T^2, and T^3 in T Region Obtained from Intensity of Signals in ^{29}Si CP/MAS NMR Spectra

organosilica	T^1	T^2	T^3
M-TMS	26.0	49.7	24.3
V-TMS	19.8	53.8	26.4
E-TMS	22.6	57.2	20.2
O-TMS	22.2	57.5	20.3
O-TMS-w	36.2	56.3	7.5

same number of surface silanols (Figure 5). This agrees with DFT results by other authors.[30] For TM−MS and M−TMS species to be of roughly the same size when reacting with the surface silanols, no condensation can have occurred in the latter before the grafting of the molecule onto the surface occurs. Condensation, which does take place in all trimethoxy silanes used in this work, occurs on the silane units already grafted onto the surface. In this regard, note that E-TMS, which is only slightly bigger than M-TMS, eliminates less surface silanols (see the Q region, Figure 5).

3.3.1. T Region of the ^{29}Si CP/MAS NMR Spectra. In the T region, signals at $\delta = -45 - -50$ ppm, $\delta = -54 - -59$ ppm, and $\delta = -63 - -69$ ppm, assigned, respectively, to mono- (T^1), di- (T^2), and tri- (T^3) fold Si−O linked silicons appear in Figure 4 (note that V−TMS signals are sequentially shifted to lower ppm). To obtain as much information as possible from the T region of the spectrum, we have undertaken a theoretical estimation of the ratio of T^1, T^2, and T^3 signals under specific situations. This was done in the following way.

F1 trialkoxysilane molecules, to be attached to the silica surface, can only adopt two configurations: either they are directly grafted to the silica or they are condensed to an alkoxysilane that on its turn is grafted to the silica. We have called these two situations F1g (directly grafted) and F1c (condensed to another alkoxysilane molecule). The same notation for higher functionalities can be used: FN_{ijk}, where N stands for the functionality 1, 2, or 3 and ijk can either be g, c, or o, where g stands for a graft to the silica surface, c stands for condensation with another silane, and o stands for a hydroxyl group.

An F2 trialkoxy molecule can adopt five configurations once it is attached directly or indirectly to the surface: $F2_{gg}$, $F2_{gc}$, $F2_{go}$, $F2_{cc}$, and $F2_{co}$. F3 molecules on their turn can adopt the following eight configurations: $F3_{ggc}$, $F3_{ggo}$, $F3_{goo}$, $F3_{gco}$, $F3_{gcc}$, $F3_{cco}$, $F3_{ccc}$, and $F3_{coo}$. Note that different FN_{ijk} will contribute to the same T^n signal, for example, $F3_{gco}$, $F3_{cco}$, and $F2_{gc}$ are T^2 signals. Now, with this notation, all possible configuration of mono-, bi-, tri-, etc. alkoxysilane (or polysiloxane) molecules can be written. A very simple example is monomolecular grafting of the trialkoxysilanes grafted onto the silica. The possible configurations are $F1_g$, $F2_{go}$, $F2_{gg}$, $F3_{goo}$, $F3_{ggo}$, and $F3_{ggg}$. In the T region, they will appear as T^1, T^1, T^2, T^1, T^2, and T^3, respectively. The same as for monomolecular alkoxysilanes has been done for bimolecular, trimolecular, and tetramolecular species (i.e., two, three, or four alkoxysilanes condensed together, at least one of them being grafted onto the surface).

This theoretical approach is forcedly rough, as the real probability of each configuration is unknown. However, being aware that a quantitative theoretical calculation of the spectra is impossible, we have made the (rough) hypothesis that all possible configurations of the silane unit have the same probability (i.e., we have only tried to identify all possible configurations and eliminate impossible ones). An example of impossible configuration is $F2_{gc}$ in a monomolecular grafting, as c implies the existence of condensation, which obviously does not occur in monomolecular grafting. We have given probability zero to $F3_{ggg}$, based on the literature.[1] The only exception to the procedure described previously has been configurations implying bidentate coordination, to which we have assigned a lower probability than to the rest of the possible configurations; this lower probability is based on the ratio of geminal to isolated silanols in Aerosil 200.

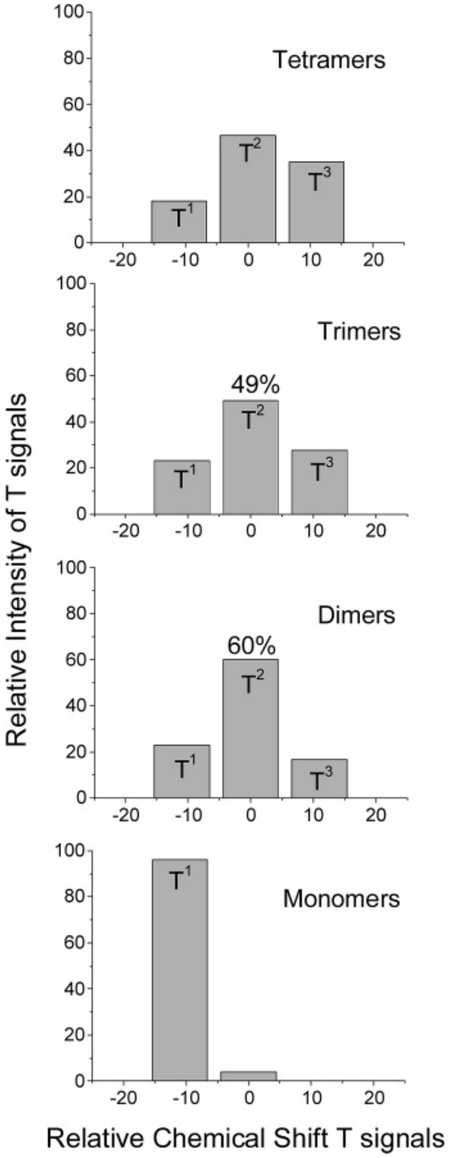


Figure 6. Calculated ratio of the contribution of T^1, T^2, and T^3 signals in mono-, bi-, tri-, and tetramolecular grafted species to the overall T signal.

The detailed development of this work is out of the scope of the present article and will be published separately. However, some of its conclusions are relevant to the characterization performed on the organosilicas described here. Table 2 presents the experimental percentage ratio of T^1, T^2, and T^3 in some of the organosilicas.

Figure 6 shows the calculated ratio of T^1, T^2, and T^3 signals in mono-, bi-, tri-, and tetramolecular grafted species obtained theroretically as explained previously.

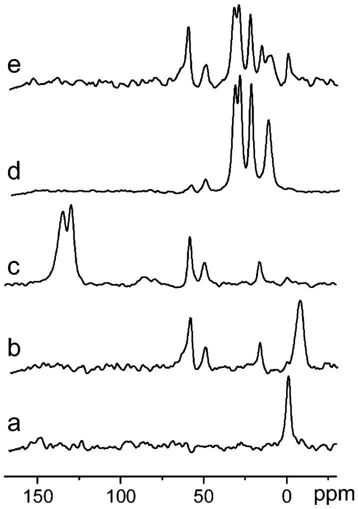


Figure 7. ^{13}C CP/MAS NMR spectra for TM-MS (a), M-TMS (b), V-TMS (c), O-TMS (d), and O-TMS-w (e) modified Aerosil 200.

Comparison of the T region spectra in Figure 4, or the percentages in Table 2, of the different organosilicas with the theoretical estimations in Figure 6 indicates that a distribution such as that shown by E-TMS and O−TMS, especially the high proportion of T^2 (near 60% of the overall T signal), must correspond to the existence of dimers and a smaller ratio of trimers. For O−TMS-w, the high T^1 values and the almost absence of T^3 are related to a distribution of monomers and dimers; the relatively high values of T^3 and low values of T^1 in V−TMS imply a condensation that is higher than in the rest and over 3. Finally, the spectrum distribution in M−TMS, with high values of T^1 and T^3 and lower values of T^2, is coherent with a distribution of species from monomers to tetramers, with the highest population being trimers.

Summarizing, the addition of PTSA results then in an increase of species condensation and an extensive reaction of surface silanols, if compared to the uncatalyzed analogues. This second point derives from the study of the ^{29}Si NMR Q region, particularly comparing the Q region of O−TMS with and without catalysis.

3.4. ^{13}C CP/MAS NMR. As seen up to now, the uncertainty regarding the average molecular weight of the trimethoxysilane derived species grafted onto the silica surface is probably the strongest drawback for a quantitative characterization of the surface structure.

The ^{13}C CP/MAS NMR spectra can provide valuable information on the structure and thus molecular weight of the average silane monomeric unit grafted onto the silica surface. Figure 7 shows some ^{13}C NMR spectra of different samples. The silica derivatized with TM−MS (Figure 7a) has only one signal attributed to the methyl groups at $\delta = -1$ ppm. Spectra b and c in Figure 7 correspond to the derivatization product of Aerosil with M−TMS and V−TMS, respectively, and both show, besides the methyl and vinyl signals, three more signals located at $\delta = 58.7$, 49.6, and 16.8 ppm for M−TMS and $\delta = 58.2$, 49.4, and 16.2 for V−TMS. The derivatization products with O−TMS in the reactions with (spectrum d) and without catalyst (spectrum e) also have these ^{13}C signals. The intensity ratio of these signals to the alkyl C signal is higher for the product obtained without catalyst. As will be shown in what follows, those signals ($\delta = 58.2$, 49.4, and 16.2) can be assigned to the nonhydrolyzed methoxy groups.

Table 3. Some Examples of Minimum and Maximum Molecular Weight Values for Average Grafted Silane Monomeric Units, Calculated According to Number of Methoxy Groups per Alkyl or Vinyl Side Chain Provided by ^{13}C NMR

organosilica	min wt (^{13}C-NMR)	max wt (^{13}C-NMR)
M-TMS	74	91
V-TMS	76	93
O-TMS	182	194
O-TMS-w	203	203

The signal at 49−50 ppm is commonly ascribed to the residual nonhydrolyzed methoxy groups,[19] and therefore, it is not expected to appear in the TM−MS product. Signals at similar chemical shifts as those mentioned previously, namely, 16 and 59 ppm, have been observed when dealing with triethoxysilanes and assigned to non-hydrolyzed ethoxy groups, physisorbed ethanol on the silica surface, or ethoxy groups directly anchored to the silica surface (as a reaction of the byproduct of the silane hydrolysis).[18,19]

Taking into account that all the derivatization products obtained in this work have been submitted to the same post-treatment, it is unlikely that physisorption of methanol (as a byproduct of the hydrolysis) or ethanol (in the purification treatment) on the silica surface happens only with trialkoxysilane and not with monoalkoxy, the spectrum of which lacks these signals. The coincidence of the chemical shifts in the derivation products with M−TMS, V−TMS, and O−TMS makes it unlikely that these signals correspond to different configurations of the bonded silanes' alkyl (or vinyl) side groups. The most likely assignment of these signals is nonhydrolyzed methoxy or ethoxy groups. Supporting this idea is the fact that in the spectrum of the O−TMS product obtained in the reaction without catalyst, these signals at 16, 49, and 59 ppm are much more intense than in the rest of the spectra and that, under these reaction conditions, a lower degree of the reagent hydrolysis is occurring.

On the other hand, if only the signal at 49 ppm was assigned to nonhydrolyzed methoxy groups, not only would the other two signals remain unexplained, but the hydrolysis degree in the derivatization products would be extremely high. Given that the ^{29}Si NMR spectra do not indicate a high degree of silane condensation and that the derivatization products are very hydrophobic, as will be shown in the next section, a high degree of hydrolysis can be ruled out.

Assuming these considerations, a quantitative analysis of the ^{13}C NMR signals can be performed that will indicate the ratio of methoxy to alkyl or vinyl carbon atoms. Being that the number of nonhydrolyzed alkoxy groups per silane molecule is known, the only source of molecular weight uncertainty derives from whether the remaining functional side groups are condensed to another alkoxysilane molecule, grafted to the surface, or in the form of a hydroxyl. Table 3 compiles the minimum and maximum possible molecular weights that are consistent with the ^{13}C NMR information.

The actual molecular weight must lie near the average of the maximum and minimum values. Making use of this average molecular weight values and the microanalysis data, the number of bonded molecules in the case of trifunctional silanes can be recalculated in a more precise way. Figure 3 has been

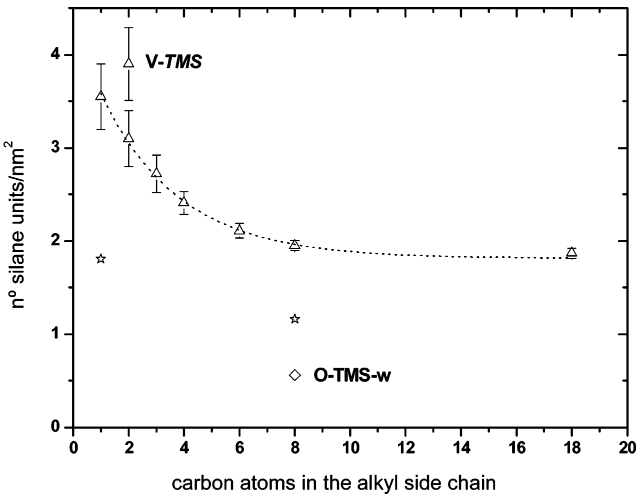


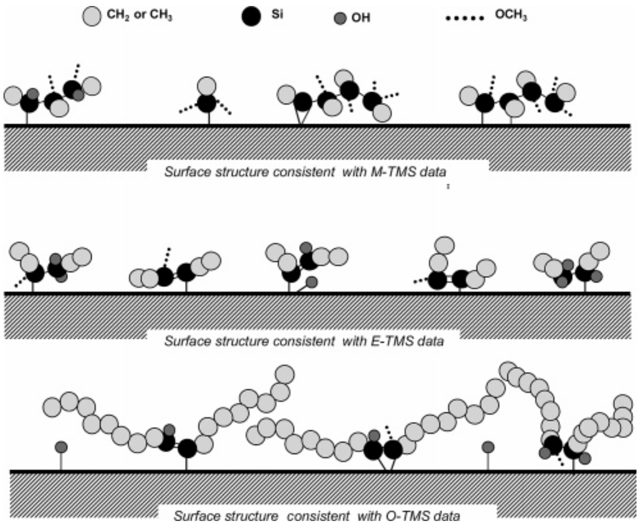
Figure 8. Number of silane units on the silica surface per nm^2 as a function of the methoxysilane alkyl chain length, making use of the molecular weight estimated by means of the ^{13}C CP/MAS NMR (Table 3 and Figure 7). Trimethoxy organosilicas (△), monoalkoxy organosilicas (☆), and uncatalyzed O-TMS-w organosilica (◇).

transformed into the less ambiguous Figure 8. Error bars in Figure 8 are mainly due to the remaining uncertainty in molecular weight.

Figure 8 depicts many interesting features. First, the alkyltrimethoxy series shows a very remarkable steric effect, which leads to the incorporation of about 3.5 molecules per nm^2 in the case of the smallest (M−TMS) member of the series, an amount that decreases quickly as the length of the alkyl side chain increases. Over six C atoms a plateau at 1.9 molecules per nm^2 is reached. V−TMS is incorporated up to 4 molecules per nm^2 (i.e., significantly more than M−TMS). These data are in very good agreement with the conclusions driven from the ratio of T signals in the ^{29}Si NMR spectra (Figure 4). The absence of catalyst reduces by four the number of molecules per nanometer squared. A very interesting datum is the number of silane units per nanometer squared incorporated by TM−MS, which is 1.8. As a monofunctional reagent, all silanes incorporated have reacted with a surface silanol, what implies that TM−MS has eliminated 1.8 silanols per nm^2. It is important to note that the number of silanols per nanometer squared in Aerosil 200 is said to range from 2 to 3.[39] The value of 1.8 is something between 60 and 90% of the total number of silanols.

At this point, the number of silane units per reacted silanol can be calculated for O−TMS and M−TMS, assuming that the number of surface silanols reacted by trifunctional and monofunctional methoxy silanes of identical alkyl side chain length is the same, which is supported by the Q region of the ^{29}Si NMR spectra. Under this assumption, the difference between the number of silane units per nanometer squared incorporated by M−TMS and TM−MS (or O−TMS and OdM-MS) (Figure 8) is due only to condensation in the case of the multifunctional reagent. Hence, by dividing the number of silane units per nanometer squared for trimethoxy reagents by the number of molecules per nanometer squared for monomethoxy reagents, the number of alkylsilane units per reacted silanol is obtained. This is 2.1 for M−TMS and 1.7 for O−TMS. The

Chart 2. Schematic Examples of Surface Structures of Three Organosilicas Based on Results[a]



[a] Results: number of silanols per nm^2, reacted silanols, average number of condensed silane units, number of silane units per reacted silanol, and methoxy groups per silane unit.

direct and inferred experimental results in this work are consistent with a number of reacting silanols close to 2. However, this does not mean that the total number of silanols is close to 2.

On the other hand, it has to be taken into account that the concepts silane units per reacting silanol, silane units per nanometer squared (Figure 8), and average number of condensed silane units (Figure 6), the first two deriving from microanalysis and the other from spectroscopy, are not conceptually the same. The number of condensed silane units refers to real molecules constituted by *n* silane entities condensed to one another, having in each of the entities the possibility to be grafted or not to a surface silanol. The average number of condensed silanes will therefore be larger (in the limit equal) to the number of silanes per reacted silanol. In this sense, the term surface coverage, which does not precisely describe the state of the surface, should be substituted by a more meaningful term, such as silane units per reacting silanol or average number of condensed silane units, or better both of them, as their knowledge leads to a deeper understanding of the surface characteristics.

3.5. Surface Structure as a Function of the Alkyl Side Chain. The efforts made in the preceding sections to characterize the surface of the organosilica in a quantitative or at least semiquantitative way and to refer to unequivocal concepts such as number of silane units per reacting silanol or average number of condensed silane units allow us to describe the surface of each of the prepared silica in the following way, by summarizing the information gathered along the work.

For M−TMS, the number of silane units per nanometer squared is 3.6, and the number of silane units per reacting silanol is the highest, 2. This means that on average, one of every two silane units is grafted to the surface. The number of condensed methoxysilane units as derived from the ^{29}Si spectra ranges from 1 to 4. From ^{13}C NMR, it has been inferred that there is one methoxy group per methyl group. Putting together all these results, the basic features of the surface structure can be envisaged; a schematic example of a surface structure consistent with the previous information appears in Chart 2.

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(39) Michael, G.; Ferch, H. *Schriftenreihe Pigmente: Grundlagen von AEROSIL (Technical Bulletin #11)*; Degussa AG: Frankfurt, Germany, 1998.

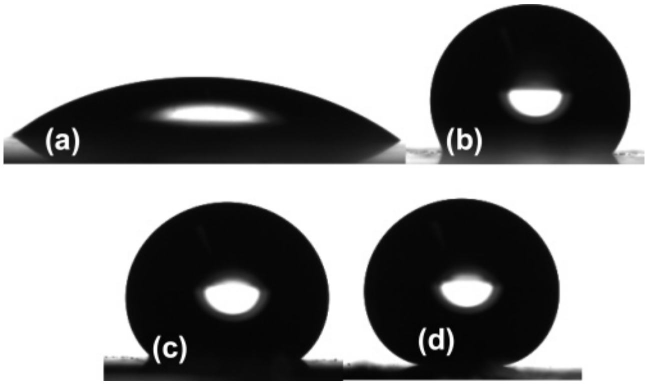


Figure 9. Water drops on AEROSIL 200 modified with O-TMS-w (a), E-TMS (b), M-TMS (c), and OdM-MS (d).

For E-TMS, the number of silane units per nanometer squared is 3.1, the number of silane units per reacting silanol will be near 2, and then of every two alkoxy units, one is grafted to the surface. The number of condensed methoxysilane units as derived from the ^{29}Si spectra is between 2 and 3, closer to 2 (dimers and trimers). From ^{13}C NMR, it has been inferred that there is one methoxy group for every three ethyl groups. As in the preceding case, a schematic example of a surface structure consistent with the previous information appears in Chart 2.

For O−TMS, data reveal that the number of silane units per nanometer squared is 2, the number of silane units per reacting silanol is 1.6, and the number of condensed methoxysilane units is between 2 and 3, closer to 2 (dimers and trimers). From ^{13}C NMR, it has been inferred that there is one methoxy group for every three octyl groups. In this last case, again a schematic example of a surface structure consistent with the previous information appears in Chart 2. For E-TMS and O−TMS, less surface silanols have reacted than in the case of the smaller M−TMS, as was concluded from the spectra in Figure 5.

The number of surface silanols reacted, the average condensation, the number of silane units per graft to the surface, the number of hydroxyl and methoxy groups, and the final ratio of the T^n signals have been considered to draw the schemes. This is only one of the many representations that can be concluded according to the characterization results; however, any representation that takes into account all of the results obtained along the characterization research will show common basic structural features with those drawn in Chart 2. The representations drawn in the chart reveal specific surface features that must manifest themselves as properties, the determination of which can help to validate the structures that are proposed in this work. The availability and accessibility of silanols seems quite characteristic of each of the organosilicas, as it appears that the most simple and adequate property is the hydrophobicity/hydrophilicity of their surfaces.

3.6. Water Contact Angle. The water contact angle of Aerosil modified with trimethoxy and monomethoxy silanes has been measured, and the results appear in Figures 9−11.

In two of the organosilicas, the water contact angles were impossible to measure, as the surface was completely water repellent and the water droplet would drift away. These were Aerosil 200 modified with TM−MS and with OD−TMS. The contact angles as a function of time for some of the samples appear in Figure 10. If the data are represented as a function of the side chain length, Figure 11 is obtained.

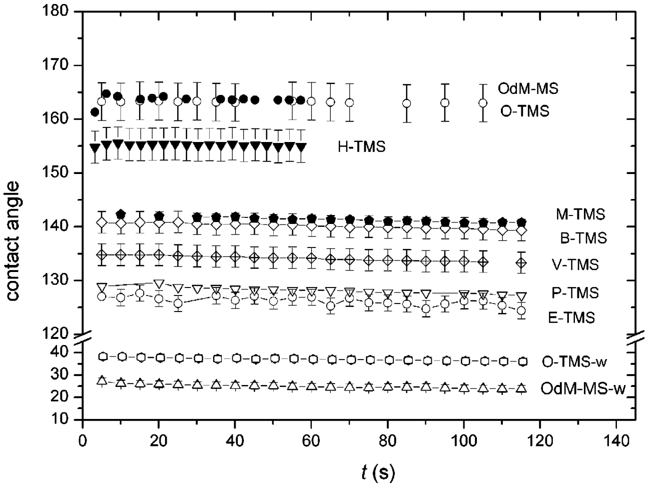


Figure 10. Advancing water contact angles as a function of time for several organically modified Aerosil 200.

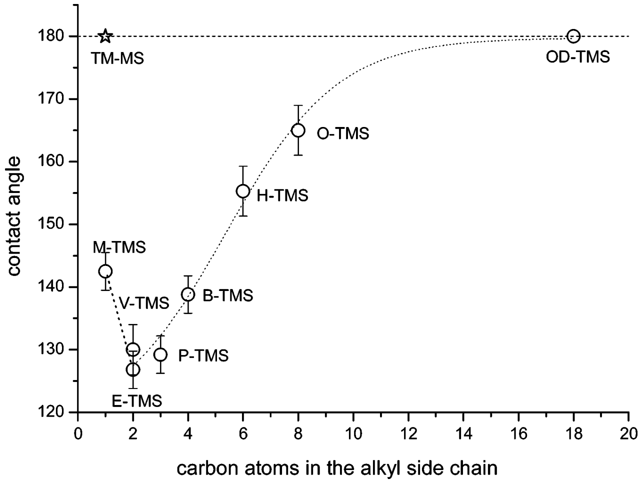
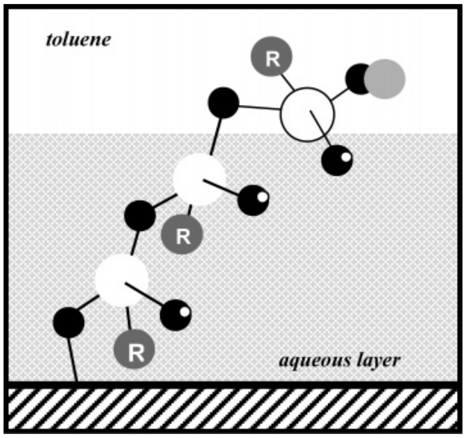


Figure 11. Advancing water contact angles as a function of the side chain weight for the modified Aerosil 200. O-TMS-w contact angle is not included because it is too low (38.2°) to be shown in the same scale.

Seven of the organosilicas prepared can be described as superhydrophobic (TM−MS, OD−TMS, O−TMS, B−TMS, H−TMS, M−TMS, and OdM-MS), as their water contact angle is over 140°; among them, two (TM−MS and OD−TMS) had contact angles over 170°. The other three (E-TMS, P−TMS, and V−TMS) can be considered hydrophobic, as their water contact angles range between 120 and 140°.

In view of the results, two causes of hydrophobicity and superhydrophobicity are identified in these materials: first, the disappearance by reaction of silica surface silanols and second, the shielding ability of a long side chain. Examples of the first are TM−MS and M−TMS, and examples of the second are O−TMS and OD−TMS, although the extreme examples of superhydrophobicity would be the silica modified with TM−MS (methyl groups as alkyl side chains) and with OD−TMS (octadecyl groups as alkyl side chains). Although these last two organosilicas are very similar regarding hydrophobicity, other surface features differ strongly. A BET study reveals that their specific surfaces are very different. Aerosil 200 modified with TM−MS is 158 $m^2\ g^{-1}$, Aerosil 200 modified with OD−TMS is 117 $m^2\ g^{-1}$, and raw Aerosil 200 is 187 $m^2\ g^{-1}$. An additional conclusion derived from these BET results is that the Aerosil surface devoid of those reacted silanols is hydrophobic.

Chart 3. Condensation of Silane Units in Silica Aqueous Layer



M−TMS is less hydrophobic than TM−MS, even though both have eliminated the same number of surface silanols (Figure 5) because TMS introduces organic silanols from the hydrolysis of the methoxy group that on their turn increase the hydrophylicity of the layer. The shielding effect is very clearly depicted in Figure 11 as a constant rise in contact angle on increasing the length of the alkyl side chain from ethyl to octyl and octadecyl trimethoxy silane. Finally, in agreement with the structures shown in Chart 2, E-TMS is less hydrophobic than M−TMS and O−TMS.

The existence of a water layer on the silica surface and of PTSA acid can explain the results obtained in this work. PTSA ($pK_a = -2.8$) is a strong organic acid, which is soluble both in water and in organic solvents; thus, added to a toluene reflux containing a suspension of undried silica particles, it is expected to be dissolved both in the organic phase and in the aqueous layer on the silica. Hydrolysis will be produced predominantly in the latter which, combined with the low (stoichiometric) concentration of methoxysilanes, may promote a step-like condensation reaction on the silica particle surface. A first trimethoxysilane hydrolyzes in the aqueous layer and reacts with a nearby silica silanol. The remaining two methoxy groups may hydrolyze and condense with eventual alkyltrimethoxysilane molecules in the vicinity. Once condensation brings the siloxane chain out of the aqueous layer, the probability of further condensation decreases, as hydrolysis becomes difficult; Chart 3 graphically depicts the proposed mechanism.

The strongly bound water layer on silica barely exceeds 0.5 nm, which may explain why in the case of small alkoxysilanes in which the alkyl side chain does not pose a strong steric hindrance, condensation progresses up to a limiting value of about four methoxysilanes (methyl and vinyl trimethoxy silane).

4. Conclusion

The modification of Aerosil 200 has been carried out using methoxysilanes in toluene reflux, with *p*-toluenesulfonic acid as a catalyst. Both trimethoxyalkyl silanes (methyl, ethyl, propyl, butyl, hexyl, octyl, and octadecyl) and trialkylmethoxy silanes (trimethyl and dimethyloctyl) have been used. When incorporating trimethoxysilanes, a plateau of modification was achieved after 1 h of reflux, while when using trialkylmethoxy silanes, a longer time of about 7 h was required. Some very remarkable features of the organophilization reaction described in this work have been shown: (i) PTSA enables a higher incorporation of methoxysilanes onto the silica in much shorter times as compared to reactions performed under the same conditions in the absence of the acid. (ii) The average number of molecules incorporated per reacted silanol varies from near two (octadecyl and octylmethoxysilanes) to almost four (vinyl and methyltrimethoxysilane). The average number of molecules incorporated to the silica per surface unit and per reacted silanol, and the number of surface silanols reacted, decreases as the alkyl side chain length increases. (iii) Seven superhydrophobic silicas were prepared, among them especially two, the contact angle of which was impossible to measure. Two structural origins for superhydrophobicity have been identified in these samples: elimination by reaction of silica surface silanols and shielding of would-be water accessible surface silanols (those remaining on the silica surface or those coming from hydrolyzed methoxy groups) by long aliphatic tails.

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