A New Solventless Process to Hydrophobize Silica Powders in Fluidized Beds

Myriam Lazghab, Khashayar Saleh, and Pierre Guigon
Dépt. Génie des Procédés Industriels, Université de Technologie de Compiègne, Centre National de Recherche Scientifique-UMR 6067-BP 20529-60205 Compiègne cedex, France

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A new hydrophobization technique was developed in a fluidized bed reactor to modify the surface of silica-based powders with n-octadecyltrichlorosilane (ODTCS). The reaction was performed at dry phase by mixing two classes of particles during the fluidization: "target-particles" to be treated (a fine microporous silica powder) and "ODTCS-carrier" particles consisting of coarser porous alumina beads containing an adequate amount of reagent. The results showed that ODTCS was successfully anchored on silica surface and achieved high surface coverage (1.4 groups/nm^2) in only few minutes with an interesting hydrophobic behavior. The energy consumption is reduced if the reaction is carried out at low temperatures, but using humidified air (7% RH). These conditions promote, however, a vertical polymerization of the reagent on solids surface. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 897–908, 2008

Keywords: hydrophobization, silanization, fluidized bed reactor, chemical grafting, wettability

Introduction

Hydrophobic oxide materials are widely used for different gas and liquid-phase separation processes. Silica is one of the most widely used solids for chromatography.[1–3] In addition, hydrophobic silica is an efficient adsorbent material for purification of biologically active compounds and medicinal preparations as well as for stabilization of multicomponent systems.[4]

Organosilanes are widely used as effective surface-modifying agents for different substrates including metal oxides with the reaction known as silanization. These organosilanes have a general formula of R_nSiX_n (with $n = 1$–3), where X is called hydrolyzable or functional group (most often chloro or alkoxy groups) and R is an alkyl group (chain of variable length responsible for the hydrophobic character).[5–7] Silanization of a silica surface provides a basis for the transformation of hydrophilic silanol groups (naturally present on the silica surface) into hydrophobic groups as follows:

$$\mathrm{SiOH} + R\mathrm{Si}X_n \leftrightarrow \mathrm{SiOSi}RX_{n-1} + \mathrm{HX}$$

This treatment lowers the affinity of modified silica with respect to water.[8] Because of robust Si—O—Si linkages, organosilanes are covalently attached to the substrate surface, and provide good thermal and chemical stability.[9]

Trifunctional organosilanes ($RSiX_3$), compared to their homologous monofunctional reagents are more reactive. However, their ability to polymerize in the presence of water leads to two different surface structures. Horizontal grafting refers to the notion that there is significant Si—O—Si bridging parallel to the silica surface (siloxane network supported by the surface). This configuration is achieved by the reaction of silanizing agents with the silica surface under

Correspondence concerning this article should be addressed to K. Saleh at Khashayar.saleh@utc.fr

anhydrous conditions. However, in the presence of water or humidity, trifunctional reagents can polymerize before their attachment to the surface.[10] This latter mechanism, known as vertical polymerization is in competition with the horizontal grafting mechanism. Nevertheless, polymeric aggregates formed by vertical polymerization could attach to the substrate at one or more points through covalent bonds.[11]

The 2D horizontal polymerization of certain long-chained trifunctional organosilane, such as *n*-OCTCS usually induces the creation of monolayers that are closely packed and highly ordered, referred to self-assembled monolayers, SAMs.[12,13] SAMs have attracted a great deal of attention in recent years due to their interesting properties as candidates for isolating interfaces and improving interfacial adhesion. This interest arises from the crucial importance of SAMs in modern nanotechnology.[1–3] In chromatography, the selectivity of stationary phase with respect to adsorbents is mainly dependent on SAMs order, mobility, flexibility, and distribution of alkyl chains bonded to surface. Direct information about the bonded phase morphology of SAMs can be obtained through spectroscopic studies (FTIR, Raman, NMR spectroscopy).

Although silica as a matrix material offers an advantage of well-characterized and uniform porous structure, modified silica has an important inherent disadvantage due to accessible residual silanols (Si—OH). These latter bring a significant specificity to the adsorption interactions (polar interactions), especially for compounds of basic nature, and are considered to be the main reason for poor reproducibility of modern hydrophobic adsorbents.[14] Consequently, "end-capping" method or treatment is generally used to achieve high alkyled-silica. In this method, residual silanols are allowed to react with a short chain organosilane such as trimethylchlorosilane (TMCS). This treatment is thoroughly described by some researchers in chromatography synthesis techniques.[15–17] However, residual silanol groups are present even in the "explicitly" hydrophobized silicas including those that undergo end-capping treatment with small silanizing agents.[18]

Generally, the methods of surface modification of inorganic particles (involving silica) with organic reagents can be basically divided into dry and wet methods. Dry or gaseous methods are usually carried out at high temperatures in order to enable the reagent to react with the surface in its vapor form.[19] However, operating at elevated temperatures narrows the application filed of those methods for surfaces that are sensitive to the temperature. In wet methods, the surface modification is carried out in an organic solvent or an aqueous solution. The reagent must be soluble in the liquid phase and there exists some problems of solvent recovery, on the one hand, and long operations, high costs, severe pollution, and low efficiency, on the other hand.[20] Then producing large amount of high hydrophobic porous silica adsorbents, with less undesirable residual silanols, and with cleaner and easier modification methods, are the main critical points in fast development of hydrophobization treatments.

The aim of this work was to test the applicability of a new process for chemical hydrophobization in a fluidized bed reactor of porous silica powders. This new process does not make use of any liquid solvent, as the reaction is performed in gaseous phase at relatively low temperatures. To produce high hydrophobic behavior and to reduce residual silanol groups, surface modification was performed using *n*-octadecyltrichlorosilane (ODTCS) followed by TMCS for end-capping treatment. The silanization was carried out in the reactor by mixing two classes of particles during the fluidization. The first class was the powder to be treated called "target particles" and the second the "reagent-carrier" particles with high porosity containing already a known amount of reagent. During the fluidization, the reagent entrapped within carrier particles is evaporated and diffuses instantaneously into the fluidized bulk. The evaporated reagent would then react with the available silanol groups of the target particles. Compared to liquid phase treatments, this process offers two main advantages. First, the reaction is faster as it occurs in gaseous phase that is characterized by higher molecular diffusivities. Moreover, the gas stream removes continually the HCl formed during the reaction and shifts the chemical equilibrium toward the desired direction. The choice of the carrier particles could be based on both their porosity (high porosity to absorb a sufficient quantity) and mean particle size (large enough to be easily separated from target particles by sieving). Note that this new hydrophobization process has been developed in our laboratory and recently patented.[21]

First, the feasibility and the performance of this new process were tested using a stream of hot dry air (110°C) to perform the fluidization. Then the effect of lower fluidization air temperatures, 80 and 60°C, with a relative humidity RH set to 7%, were tested. The organization and the order of the various self-assembly monolayer formed were then assessed.

Material and Methods

Porous silica powder and reagents

Silica powder was purchased from Echochrom (MP Silica 63-200 Active 6 Å). The particle mean size was 162 μm and its specific surface area measured by nitrogen adsorption method (BET) was about 480 m^2/g. The internal mean pore size was 6 nm.

Two chloro-organosilanes were used for the surface modification. The first one was *n*-octadecyltrichlorosilane $CH_3(CH_2)_{17}SiCl_3$ (ODTCS). It is a reagent with three chlores as functional group and with one long alkyled chain containing 18 carbon atoms, responsible for the hydrophobic behavior. The ODTCS is an organosilane with a relatively low vapor pressure. The second reagent was the trimethylchlorosilane 99% C_3H_9ClSi (TMCS), a reagent often used for end-capping of silica in organic solvents. Contrary to ODTCS, TMCS reagent has a relatively higher vapor pressure (25,000 Pa at 20°C) that let it readily fairly reactive even at room temperature.

Fluidized bed reactor

The fluidized bed set-up used in this study is presented in Figure 1. The reactor was 0.5 m in length and 0.1 m in internal diameter (⑦). Temperature, hygrometry, and pressure control probes are evenly positioned along the reactor and connected to a data acquisition system (⑧). The reactor is supplied by air that can be heated to the desired temperature using electrical heating elements (④), regulated by a control system (⑥). Before heating, the air can be either humidified

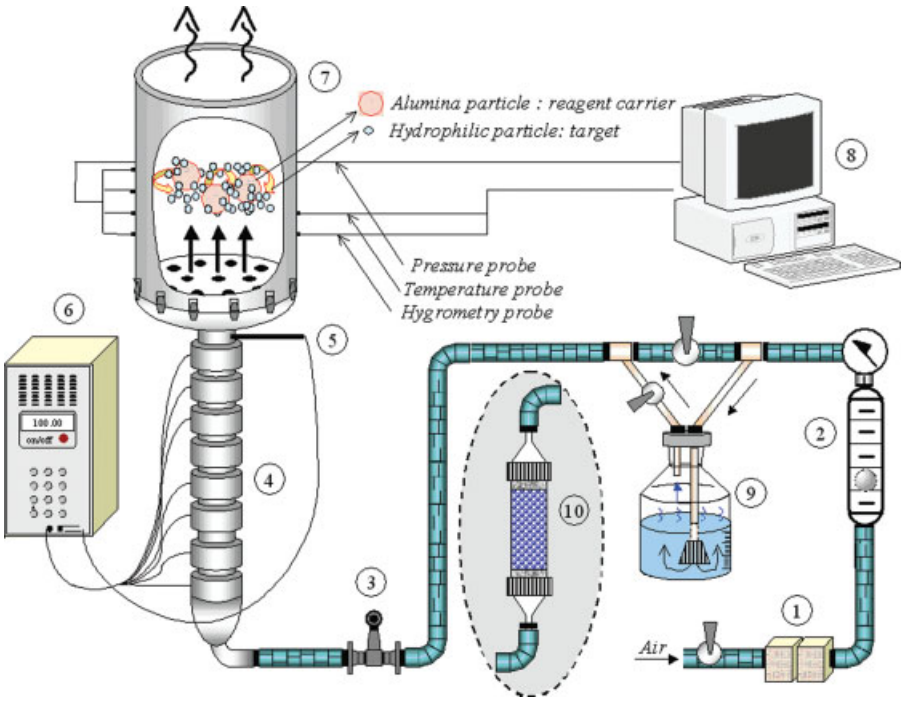

Figure 1. Schematic presentation of the fluidized bed set up.

(1) Air filter, (2 and 3) air flowmeters, (4) "O-ring" electrical heaters (20–350°C), (5) "K" thermo probe, (6) temperature control system, (7) stainless steel fluidized bed reactor, (8) data acquisition system, (9) humidification system (7% RH to 50% RH), (10) drying system filled with well-regenerated silica gel particles (can replace 9). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

using a bubbling water system (⑨), or dried using a fixed bed of silica gel (⑩).

Experimental procedure

The silanization reaction was carried out in the reactor by mixing two classes of particles during their fluidization in the reactor (Figure 1).[24] Alumina particles with relatively high porosity and particle mean size ranging between 0.5 and 1 mm were used in this study as the reagent carrier. Before use, the particles were rinsed by distilled water and oven-dried (24 h at 180°C and 20 mm Hg). The particles were soaked beforehand in the reagent, and so contained a known quantity of ODTCS or TMCS.

The silica powder was used as target particles. 125 g (~500 ml) of silica was first fluidized in the reactor. When the temperature and the relative humidity of air reached the desired values, alumina carrier particles containing already a known quantity of organosilane was added to the reactor. The amount of reagent added with respect to silica was fixed at 50% w/w for ODTCS and 20% w/w for TMCS. Some silica samples were removed from the reactor during the fluidization for analysis. To minimize the change of temperature due to adding the reagent, alumina carrier particles were put in a small hermetic vessel and kept inside an oven at the same temperature as the operation. Doing so, the temperature variations of the fluidized bed reactor did not exceed ±3°C during a period of 1–2 min. In addition, to not disturb the conditions of silica powder modification, the particles of alumina withdrawn while sampling were systematically sieved and recycled rapidly into the reactor.

The fluidization air velocity was set to 0.1 m/s for all experiments. This velocity was largely higher than the complete fluidization velocity of the particles mixture, that is, the air velocity required to fluidize homogeneously the two classes of particles. According to the correlation proposed by Zergueras,[22] the complete fluidization velocity in our conditions is estimated at 0.03 m/s.

Surface modification assessment

Some tests were performed on samples withdrawn during fluidization and/or at the end of the operation. Hydrophobic behavior of samples was assessed by wettability tests. Two techniques were used: contact angle measurement and mass variation due to water vapor sorption.

• Contact angle θ, was assessed by capillary rise kinetics measurement through a packed bed of tested powder, using Washburn model[23]:

$$\frac{h^2}{t} = \frac{r_{\text{eff}}\gamma_{\text{lv}}\cos\theta}{2\eta}, \tag{1}$$

where h is the height of liquid risen through the packed powder bed after a time t. Parameters ρ, γ_{lv}, and η are the wetting liquid's density, surface tension and viscosity, respectively. r_{eff} is the effective capillary radius which can be considered as the geometric constant of the p bed.

A known quantity of silica powder (1.5 g) was regularly tapped into a tube (1 cm in diameter and 5 cm length and plugged in one end with a thin hydrophilic paper disc) until a constant height was obtained. The packed tube was hung up to a microbalance related to a data acquisition system (Capillary rise UK SMS tensiometer). A liquid test was then brought into contact with the tapped tube and silica mass uptake was automatically registered. θ was calculated using the two liquids test method. A wholly wetting liquid, for example, hexane was first used to measure the capillary rise kinetics in complete wetting conditions[24] ($\cos\theta = 1$). Further to this first step, the packed bed of powder was gently heated to evaporate the wetting liquid (40°C for 24 h). When the hexane was utterly evaporated from the bed, the experiment was performed using the test wetting liquid (water). Doing so, there is no need for direct determination of the effective capillary radius, r_{eff}, required for liquid rise rate calculation in Washburn equation. More details on θ calculations using two liquid tests can be found elsewhere.[25,26]

• The hydrophobic level of treated samples was also evaluated by means of water vapor sorption tests using a dynamic vapor sorption apparatus (DVS UK SMS Instruments). This apparatus consists of a twin pan microbalance with a high resolution (0.1 Ag T1%), housed inside a temperature-controlled incubator. A given amount of the solid product (10–50 mg) is placed in the sample holder and suspended to one side of the balance, whereas a reference holder is suspended to the other side. The desired humidity of carrier gas (usually nitrogen) is achieved by mixing dry and humid gas flows in the correct proportions using automated mass flow controllers. The gas is divided into two equal parts, flowing past the sample holder and the reference holder. To reduce uncertainties caused by vapor adsorption/desorption on sample holder's wall, the net liquid uptake is determined by comparing the sample holder to the reference holder. Continuous monitoring of the sample weight permits to follow the liquid adsorption from the beginning up to equilibrium. Before being exposed to any vapor, the samples are equilibrated at 0% RH to remove any surface adsorbed vapor and to establish a dry mass baseline. Next, the samples are exposed to carrier gas and the relative humidity is increased step by step during adsorption and decreased during desorption. At each step, the sample mass is allowed to reach equilibrium before humidity is varied. Obviously, higher the sample mass variation, more important are the hydrophilic interactions.[26]

In addition to these two tests, the surface coverage of samples was also calculated from carbon elementary analysis (a flash AE1112 ThermoFinnigan, sample mass 0.8–1.2 mg). Elsewhere, the grafting and the assembling mode of organic species at the surface were examined by RMN and FTIR infrared spectroscopy and by AFM analysis.

The RMN used was a carbon/hydrogen ^{1}H-^{13}C/MAS mass spectroscopy (Bruker Avance-400 MHz ^{1}H-^{13}C/MAS RMN). An infrared spectroscopy with Attenuated Total Reflection (Thermo-Nicolet IR200 ATR) was used. One hundred twenty-eight scans were performed between 4000 and 600 cm^{-1} with 4 cm^{-1} resolutions.

AFM analysis was also performed with a Nano Scope Dimension 3100 Controller Digital Microscope. Scans of the cantilever were operating with a 0° angle in tapping mode with 0.2 μm/s rate (1 Hz).

Results and Discussion

Silica powder grafted with ODTCS and TMCS

To achieve a high surface coverage, silica powder was modified in two steps using the end-capping method described earlier. In the first step, the powder was modified by adding alumina particles containing 50% of ODTCS (weight percent with respect to silica). The additional silanization time with ODTCS was set to 30 min. In the second step, another amount of alumina particles holding 20% of TMCS (weight of silica) was added to fluidized bulk. The time of silanization was set to 15 min (total time of modification = 45 min). These times were previously determined through TGA analysis to avoid any competitive silanization reactions between ODTCS and TMCS molecules on the surface.

Three different operational conditions were tested in order to study the effect of temperature and relative humidity on the process. First, the fluidization was performed using a dry air stream. Because of high hygroscopic nature of silica and in order to completely eliminate the water adsorbed by silica, it was necessary to operate at a high temperature (110°C). Then, we tried to reduce the temperature of the process to 80 and 65°C with humidified air (7% RH). Three experiments were conducted for each condition.

Grafting kinetics and surface coverage measurements

Figure 2 presents the thermograms obtained by a thermogravimetric analyzer (TGA92, SETARAM) for silica samples removed at different time intervals from the bed. The slight mass variation observed for the untreated sample ($t = 0$) that takes place around 100°C could be attributed to the evaporation of water adsorbed during the period between the sample removal and the sample analyzing. These results show that the process concerned by this study leads to a very interesting grafting efficiencies up to 25% by mass. The grafting effect is observable from the first minute of operation and becomes almost complete after 30–45 min.

In addition, the surface coverage or grafting density τ (μmol/m^2) was calculated from elementary carbon analyses. Supposing that the grafted reagent forms a molecular monolayer on the surface of silica support, the overall grafting density can be estimated using the following equation[14,27–29]:

$$\tau = \frac{\%C \times 10^6}{12.011 \times n_C \times S_{BET}\left[100 - \left(\frac{\%C}{12.011 \times n_C}\right)(M - M_{L.group})\right]} \quad (2)$$

where $\%C$ is the carbon percentage in the sample; 12.011 is the molecular weight of carbon (g/mol); n_c is the number of carbon in the grafted molecule; S_{BET} is the specific surface area of the silica powder analyzed using nitrogen adsorption by BET method (m^2/g); M is the molecular weight of the organosilane reagent (g/mol) and $M_{L;group}$ is the molecular weight of the leaving group released during the silanization (here Cl).

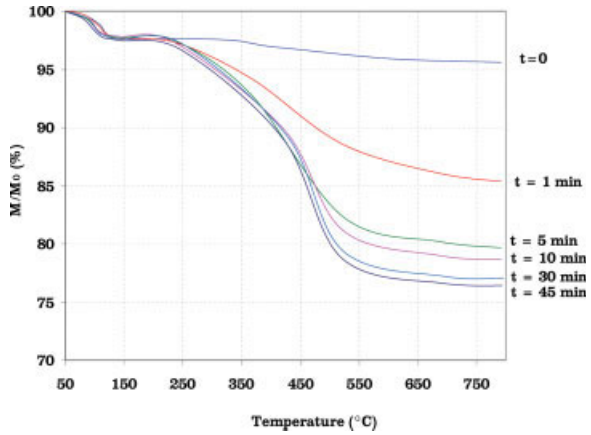

Figure 2. Thermograms of modified silica samples obtained at different operating times (Reagents: ODTCS until 30 min. and TMCS between 30 and 45 min., Fluidizing air temperature, *T* : 110°C).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The kinetics of molecule grafting and surface coverage of silica powder modified at 110°C, 80°C and 7% RH and 65°C and 7% RH, were respectively calculated. The results are given in Figure 3. As it is shown in this figure, the surface grafting density, τ_{ODTCS}, in the three conditions of silica modifications mentioned above, increases as soon as the ODTCS is introduced in the reactor. The grafting density is then stabilized roughly around its maximum value, that is, 2.2 μmol/m^2 after 10 min at 110°C, 2.8 μmol/m^2 after 30 min at 80°C, and 2.1 μmol/m^2 after 30 min at 65°C. According to Helmy and Fadeev,[29] the silanization process seems to be characterized by two distinct steps. The initial process is a relatively rapid growth in grafting density, where all silanol groups are available. This step is followed by a rather slow period process, where less silanol groups are accessible to the new incoming ODTCS. This decrease in reaction rate can be attributed to molecular steric hindrance of the already grafted molecules. The surface coverage approaches, thus, its maximum value.

Furthermore, we note that silica modified at 110°C needed the shortest time to achieve its maximal grafting density. This can be explained in the one hand by the effect of the temperature on the reaction rate (Arrhenius law); and on the other hand by the action of water molecules on the reaction. Indeed, water affects considerably silanization rate and ODTCS condensation mode. In dry air, ODTCS reacts directly with silanol groups with HCl released as by-product. In contrary, in wet air the chlore groups of ODTCS are first hydrolyzed to form octadecyltrihydroxylsilane ($CH_3(CH_2)_{17}SiOH_3$) that condense due to hydrogen bonds and van der Waals interactions to form clusters before reacting with the surface. Finally, the clusters react with the silanol groups of silica surface with water molecule release.[29] Thus, silica modified at 80 and 65°C take more time to achieve their maximal grafting density. As it will be described later, in that case water molecules promote the ODTCS vertical polymerization and accordingly the carbon percentage increases. Although in dry air and high temperature (110°C), ODTCS reacts rapidly with the silica surface and polymerizes rather horizontally in monolayer pattern. That monolayer organization or self-assembling monolayer (SAM) exhibits very interesting hydrophobic behavior.

Furthermore, it should be noticed that Eq. 2 is only applicable for a monolayer-grafted of reagent. Thus, when the vertical polymerization takes place (at low temperatures 80 and 65°C), this equation is not straightforwardly valid for silica modified, and τ_{ODTCS} values are just given for indication. Although the mechanism of reaction appears to be similar in humid condition (7% RH), the product treated at 80°C, acquires a higher grafting density than the product treated at 65°C. This fact could be explained by two phenomena which may coexist. On the one hand, increasing the temperature leads, at the same time, to a higher reaction rate and to a rise of reagent concentration due to a higher evaporation rate. On the other hand, for the same relative humidity, the absolute humidity (i.e., the amount of water vapor available in the reactor)

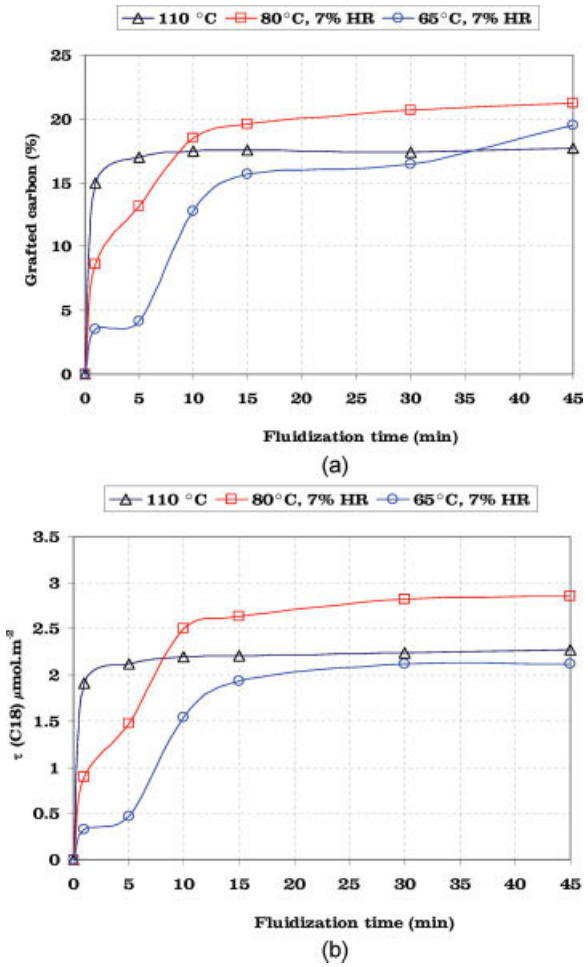

Figure 3. Evolution of grafted carbon percentage (a) and grafting density τ_{ODTCS} (b) as a function of operating time.

(50% of ODTCS and 20% of TMCS at [80°C; 7% RH], [65°C; 7% RH] and at 110°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

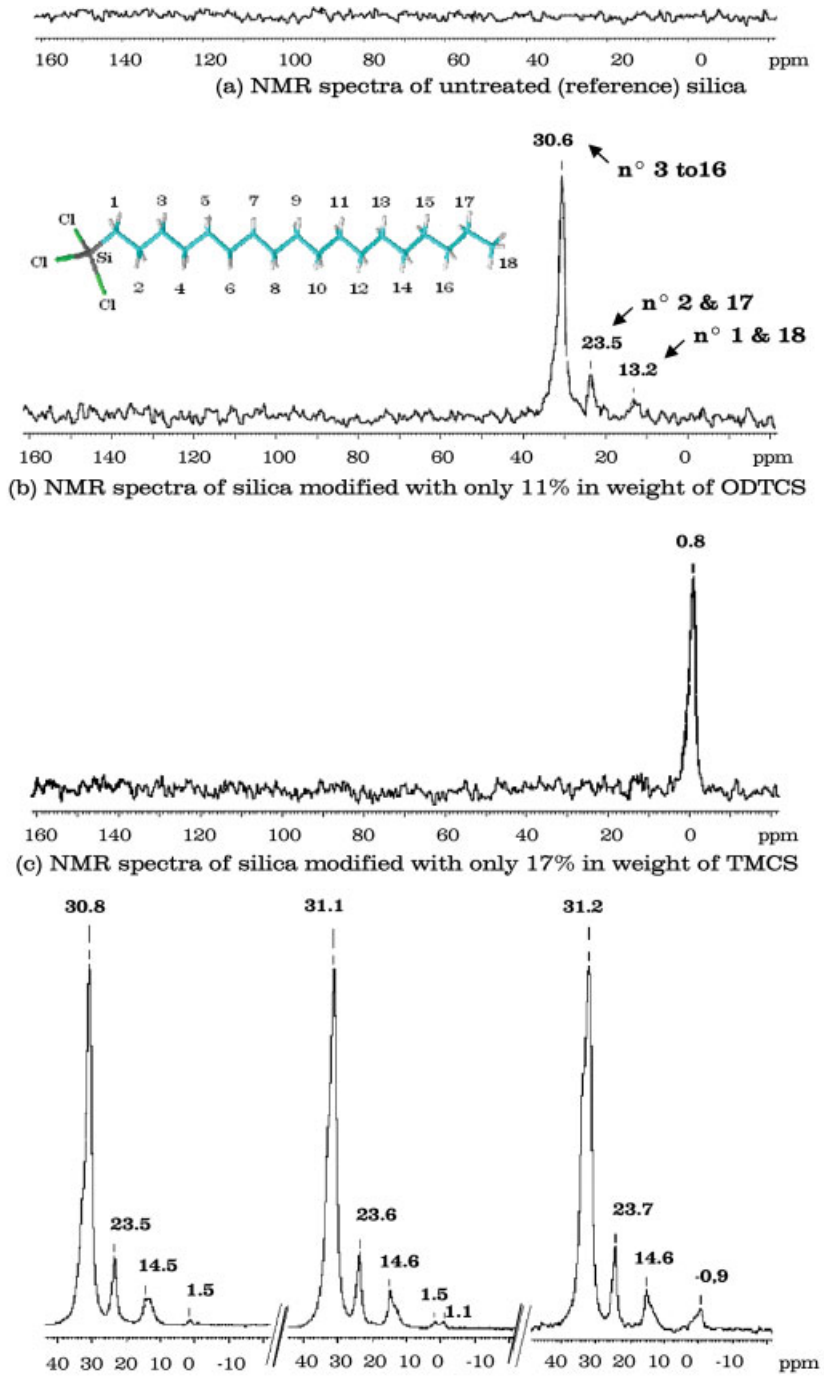

Figure 4. ^{1}H-^{13}C solid state NMR spectra of modified silica in fluidized bed by ODTCS and TMCS (2 ms contact time and 10 kHz sample rotation frequency).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increases with the temperature. Since the water acts as a catalyst for polymerization, this effect is favorable to reaction.

Figure 3 also shows that the addition of TMCS could revive grafted carbon percentage. However, this grafting resumption is almost insignificant and only perceptible for the experiments conducted at 65°C. Indeed, Figure 3a shows that elementary carbon percentage for this experiment increases from 17 to 19% after addition of TMCS, whereas for two other conditions this parameter remains constant. This observation may confirm the hypothesis that at those conditions the vertical grafting is the predominant mechanism of reaction and consequently there are more silanol groups available for TMCS grafting during the end-capping step.

Note that for silica modified at 110°C, the grafting density, τ_{ODTCS}, was about 2.18 μmol/m^2 after only 10 min of silanization and τ_{TMCS} was 0.125 μmol/m^2. This surface overlay matches 1.36 ODTCS groups/nm^2 and 0.07 TMCS groups/nm^2, then a total of 1.43 groups/nm^2 of grafted silanol species. Cao et al.[30] silanized a porous silica powder with almost the same characteristics as that used in this study (BET surface area $\approx$ 500 m^2/g and 6 nm pore size) using a trialkylsilane in supercritical CO_2 solvent at 70°C. They found a grafting density of 1.6 groups/nm^2 after 24 h of treatment. Moreover, some authors had highlighted that 1.6 groups/nm^2 is the maximum surface coverage value for any small-pore size particle substrates.[31–33] Hence, the silanization in fluidized bed reactor presents an overriding advantage of shortening the process time and attain high surface coverage value.

Determination of predominant grafting mode

To bear out the chemical grafting on surface of both ODTCS and TMCS discussed earlier, solid-state ^{13}C-NMR analysis was performed on modified silica samples. Likewise, two other silanization runs were carried out on silica using each of reagents separately (11% ODTCS and 17% TMCS, respectively). These two separately modified silica were necessary to identify the NMR spectra. Results are shown in Figure 4.

We had to identify the different NMR carbon shifts of ODTCS on modified silica to those reported by Gao and Reven[34] (Figure 4b), where ODTCS is chemically adsorbed to the surface. In comparison with nongrafted silica (Figure 4a), we note three peaks appearance around 30.6, 23.5, and 13.2 ppm (Figure 4b). These peaks match closely to carbon shifts in position 3 to 16, positions 2 and 17, and positions 1 and 18 in ODTCS molecule, respectively.[34–36] A NMR shift identification alike ODTCS was performed on NMR spectra of TMCS reacted with silica powder. Results were compared to those obtained from Silva et al.[37] (Figure 4b) and Tao and Maciel.[38]

The shift of 0.8 ppm shown in Figure 4c is comparable to that mentioned by these authors for TMCS chemically grafted to silica surface ($\approx$0 ppm). The assorted carbon shift identifications of ODTCS and TMCS NMR spectra permitted to confirm that reagents were not physically adsorbed but chemically grafted to silica surface.

NMR spectra of silica modified in fluidized bed at various temperatures with ODTCS and TMCS successively are presented in Figure 4d. As it is shown for the three temperature conditions, we note carbon shifts corresponding to ODTCS molecule chemically grafted to silica surface. Characteristic shift of TMCS directly grafted to the surface (0.9 ppm) was found for silica modified at 65°C and 7% RH only. Although silica modified at 110°C had 1.5 ppm as TMCS carbons shift, which probably signify that TMCS is indirectly bonded to the surface. In other words, TMCS might be grafted to the polymerized ODTCS layer. At last, silica modified at 80°C and 7% RH shows two distinguished TMCS carbon shifts in NMR spectra (1.5 and 1.1 ppm). Thus, it can be concluded that TMCS molecules could be grafted both directly and indirectly to silica surface.

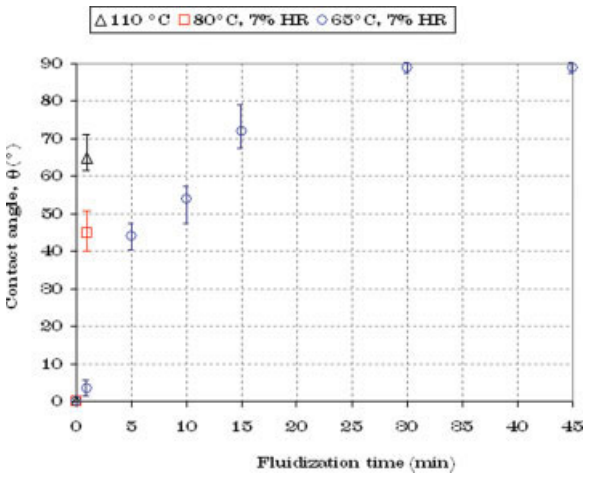

Figure 5. Evolution of solid–liquid contact angle with the operating time for silica modified at different conditions.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Wettability of modified silica

The modification of wetting behavior of samples after silanization at different conditions was quantified by two wettability assessment methods.

Liquid–solid contact angles

Liquid–solid contact angles obtained from capillary rise measurements are presented in Figure 5 (θ measurements were run three times). As it can be noted, an abrupt increase in contact angle is observed for silica modified at 110 and 80°C from the first minute of fluidization ($\theta \approx 66^\circ$ and $\theta \approx 47^\circ$, respectively). For following points (not presented), the silica samples were so hydrophobic that there was no spontaneous water rise through the packed powder bed. The contact angle, θ, presumably exceeds 90°, the maximum that can be measured using capillary rise method.

For silica modified at 60°C and 7 RH%, the contact angle measured at the first minute of fluidization is too lower compared to the two other cases ($\theta \approx 4^\circ$). Contact angle increases slowly and reach the maximum (90°) after around 30 min. Hence, silica modified at 60°C exhibits a shaded hydrophobic behavior with fluidization time. Even the samples show a macroscopic hydrophobic behavior, they still involve certainly some polar interacting sites. Then, the achieved hydrophobic level is assumed to be inferior to that obtained for silica modified at 110 and 80°C. Note that the capillary rise results are congruent with the grafting kinetics and mode of ODTCS presented above.

DVS analysis

To better classify the hydrophobic level obtained in each condition, we analyzed samples in various relative humidity atmosphere (from completely dry 0% to very humid atmosphere, 90% RH at 20°C). Analyses were performed with water vapor sorption and desorption, successively. The corresponding results (Figure 6) indicate that all samples exhibit a

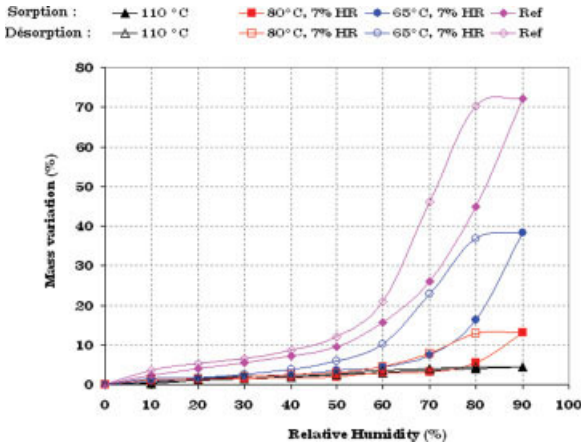

Figure 6. Sorption–desorption isotherms of silica measured at 20°C using DVS device.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hysteresis loop, the lower branch of which represents measurements obtained during water adsorption and the upper branch during desorption. It is well-established that such a hysteresis loop is related to the filling and emptying of the mesopores by capillary condensation. It can be seen that untreated silica (labeled Ref. in Figure 6) adsorbs substantial amounts of water, up to 72% by mass at 90% RH and at 20°C. According to IUPAC classification, the hysteresis loop of untreated sample is a classical Type IV (i.e., concave to RH% axis at low relative humidity, then almost linear and finally convex at high relative humidity) which is characteristic of customary mesoporous supports.

Contrary to the untreated reference sample, the silica modified at 110°C shows no significant mass change even at very high relative humidity (maximum $\approx$ 4% mass variation in 90% RH vs. 72% for the control). The silanization with ODTCS and TMCS at 110°C seems to provide a close packed monolayer horizontally grafted to the both internal and external surface of the solid. That reagent organization is responsible for such a high water repellent behavior, and leaves few hydrophilic sites able to undergo polar interactions. The capillary condensation phenomenon is inhibited because the pores interface is poorly wetted by water.

Finally, vertical polymerization proposed previously for silica powders modified at 80°C and at 65°C with 7% RH is in agreement with DVS results. Indeed, even though the apparent surface coverage is significant for silica modified at 80°C, the ODTCS vertical polymerization does not permit to mask completely the residual hydrophilic groups. Consequently, despite the hydrophobic effect that is still obvious for samples treated at 80 and 65°C, the outcome is less pronounced compared to the product obtained at 110°C. Thus, a decrease of the temperature coupled with humidification promotes vertical ODTCS growth and contributes only slightly in covering the residual silanol sites. It is also interesting to note that the hysteresis loops of these two samples are of Type V rather than Type IV (i.e., they are convex to the RH% axis over the complete range with no initial uptake). According to the literature, this type of hysteresis is indicative of weak adsorbent–adsorbate interactions, which is not surprising in our case and can be easily explained by promoted hydrophobic effect. Moreover, as the operating temperature increases from 65 to 80°C, the beginning of hysteresis loop is shifted toward higher RH values and the vapor sorption is reduced. Indeed, the sample treated at 80°C shows a hydrophobic behavior similar to that obtained for powder modified at 110°C until ~70 RH%. Beyond this value, the uptake rises more quickly to attain 13% at 90% RH. As for the powder modified at 65°C, it can adsorb much more water vapor (38% at 90% RH) and the adsorption curve takes off at lower RH values. This behavior indicates that due to higher grafting density achieved at 80°C, fewer pores (especially the largest ones) are accessible to water molecules. The Kelvin radius (and consequently the corresponding RH% value) involved by the capillary condensation phenomenon is, hence, increased.

Organization of grafted groups in microscopic scale

Some thorough surface analyses were necessary to understand the way that ODTCS and TMCS layer organization affect the surface behavior. To verify whether a self-assembling monolayer (SAM) on silica was obtained at 110°C, some AFM surface scanning, NMR, and IR spectroscopy analyses were carried out.

AFM analysis

Both non treated silica and silica modified at three temperatures used in this study were scanned in AFM microscope. The surface of raw silica particle reveals already some roughness as it is depicted on AFM image presented in Figure 7. One can observe that the surface of silica sample modified at 110°C was quite overlaid by a thin layer (raw surface roughness buried). Moreover, one can note conspicuously that grafted layer forms a continuous layer on surface, but with an uneven rather than a regular thickness. Whereas on surface modified at 80°C, vertical ODTCS polymerization yields distinctly inter-connected island-like clusters with important layer roughness; and yields a scattered one for surface modified at 60°C.

Though ODTCS was successfully grafted on porous silica in fluidized bed, it seems to be quite difficult to establish ODTCS SAMs with regular thickness. Hair and Tripp[39] had highlighted that SAMs are difficult to perform even in very dry atmosphere. Hence, the well ordered and regular ODTCS SAMs do not really match the ODTCS layer formed on silica silanized at 110°C. Besides silanization conditions and ODTCS steric hindrance, further factors such as ODTCS alkyl chain flexibility and surface raw roughness could explain that configuration.

It was established theoretically and experimentally that some molecules are not perpendicularly grafted on the surface but are dimly tilted[40] (Figure 8). The tilt angle (β) is dependent on reagent grafting density, grafted layer thickness, alkyl chain length, and leaving groups numbers.[41] Considering that ODTCS grafting density is not presumably identical on each point, by tilting its alkyl chain ODTCS molecule can reach the neighboring groups and react with through lateral Si—O—Si bonds (self-assembling). Such chains tilting permits to the initially grafted clusters of ODTCS to

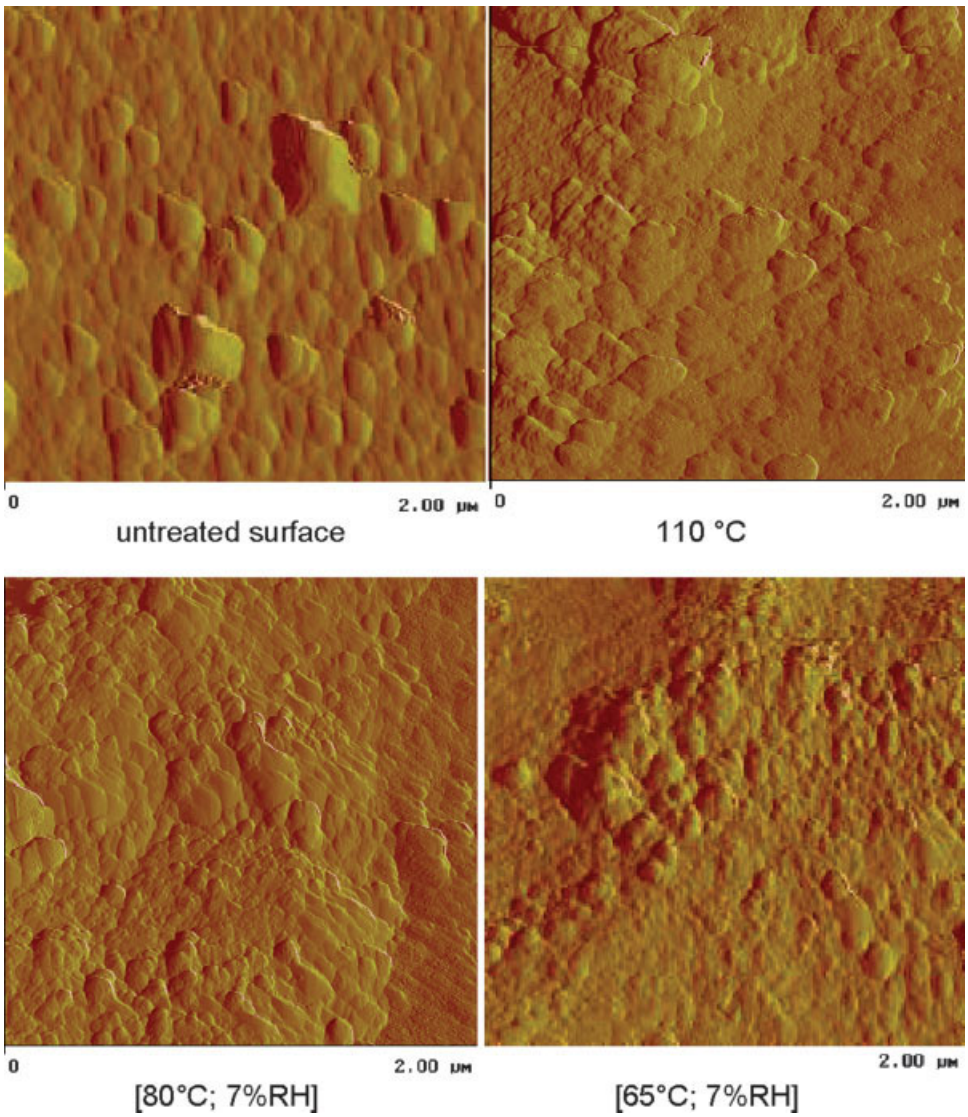

Figure 7. AFM surface analyses of untreated and modified silica.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

interconnect and achieve close packing layer (horizontal polymerization).

Raw roughness of the silica surface can also affect ODTCS alkyl chain tilting. Hostetler et al.[42] demonstrated that the higher was the surface roughness, the more irregular SAM organization was. Surface roughness or imperfections increase free volumes between ODTCS molecules, accordingly, they are less close and cannot readily interconnect. That could drive to some faint discontinuity in SAM layer with a wavy pattern.

Ordered or disordered grafted chains?

The degree of ordering in grafted molecules of long-chained alkyls may be assessed from the position of the $-CH_2$ stretching in IR and/or of the $-CH_2$ shifting in NMR scans. For utterly well ordered ODTCS SAMs, as depicted in Figure 8, the values are close to that of crystalline alkanes:

- IR scans: ν_a(2915–2920 cm^{-1} (antisymmetric stretching mode) and ν_s(2850–2860 cm^{-1} (symmetric stretching mode).[43–46]
- NMR scan: 33–34 ppm.[46–48]

Whereas for a completely disordered structure, the $-CH_2$ IR frequency stretching or NMR shifting values are close to that of liquid alkane (ODTCS in solution):

- IR scans: ν_a(2924–2928 cm^{-1} [34,48,49]
- NMR scan: 30–31 ppm[35,36,50]

The aforementioned spectroscopy scans of $-CH_2$ found for silica modified in three conditions are summarized in Table 1. Full FTIR spectra are given in appendix (Figures A1–A3).

From both $-CH_2$ spectroscopy scans and in comparison with the aforementioned values, one can find out that values are included in the range standing nearly between the superior limit of the completely well ordered SAMs and the inferior limit of the completely disordered ODTCS. Minor differences exist between values obtained for the three modified

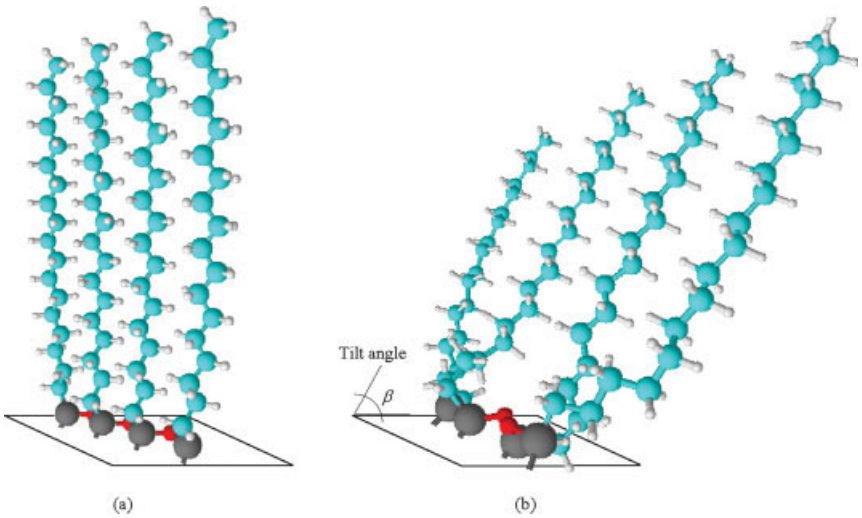

Figure 8. Schematic pattern of well-ordered ODTCS SAM (a) and well-ordered ODTCS SAM with β tilt angle (b) grafted on flat silica surface (Adapted from Cai[41]).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. FTIR and RMN $-CH_2$ Spectroscopy Scans for Silica Modified at Three Temperatures

	$-CH_2$ FTIR Frequency (cm^{-1})		
Silica Modification Conditions	ν_a	ν_s	^1H-^{13}C/RMN $-CH_2$ Shift (ppm)
110°C	2923	2850	30.9
80°C 7% HR	2921	2850	31.1
65°C 7% HR	2922	2850	31.2

silica samples. Then the arrangement of grafted molecules is assuming to be practically similar for three modified silica.

Further researchers had pointed out that on very smooth and flat surface, the outright straighten up of long alkyl chains is dependent on high grafting reagent density (~5 reagent groups/nm^2) and on carbon number (minimum 10 carbons). In such a case, besides Si—O—Si lateral bonds, the utter chains straighten up is ensured by van der Waals inter-

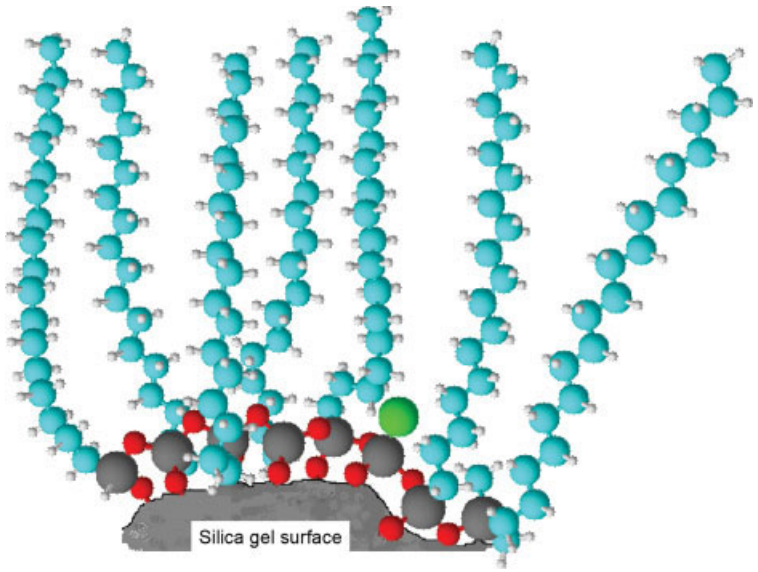

Figure 9. Schematic model of semiordered ODTCS SAM overlaid on porous silica surface modified in different temperatures (Adapted from Kulkarnih et al.[53] and Sindorf and Maciel[54]).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

actions. The more ODTCS are close-packed, the more intense are these interactions and the more leveled will be the alkyl chains, yielding to a regular thickness of SAMs.[51–54]

Because of the surface curvy and roughness (showed in AFM analysis on raw silica) and because of the low achieved ODTCS grafting density (1.4 groups/nm^2 in comparison to 5 groups/nm^2 for a flat one), well-ordered ODTCS SAMs with regular thickness seem to be difficult to obtain on porous silica particles in fluidized bed reactor at low temperatures. Thus both ordered and disordered grafted molecules might coexist on modified silica (Figure 9) with more or less extent, even for that modified at 110°C.

Conclusion

The surface modification of a porous silica powder with ODTCS trichlororganosilane is feasible in dry phase using a new technique in fluidized bed reactor. The main advantage of this new process is to avoid the use of organic solvents for silanization. The silanization reaction was carried out in the reactor by mixing two classes of particles during the fluidization: ''ODTCS-carrier'' and silica ''target'' particles. Modification of 125 g of silica powder in three temperatures of fluidization air was tested using 50% w/w of octadecyltrichlorosilane (ODTCS) and 20% w/w of TMCS. NMR analysis permitted to validate that reagents were chemically embedded to silica surface.

It was established that silanization carried out at 110°C and completely dry conditions yields to a very high ODTCS surface coverage close to the maximum value reported in literature for porous silica treated in liquid organic solvents. Besides, ODTCS grafting reaction seems to be instantaneous and leveled off rapidly after only few minutes of fluidization. The silanization in fluidized bed reactor presents an overriding advantage of shortening process time and achieve high surface coverage. Moreover, AFM scan showed that at high temperatures ODTCS SAMs overlay quite homogenously the samples surface. Wettability tests showed also that ODTCS was successfully grafted into the accessible inner sides of silica pores; which significantly reduces polar interactions in highly wet atmosphere.

It was also shown that the energy consumption can be reduced by favoring ODTCS vertical polymerization on samples in presence of water trace (7% RH). Even the ODTCS grafted quantities were the highest, ODTCS cluster vertically due to polymerization and do not utterly masks the residual silanols. Finally, reducing the temperature to 65°C gave a not attractive hydrophobic silica behavior.

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Appendix

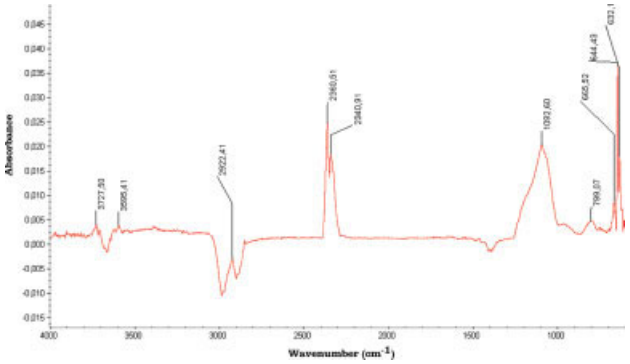

Figure A1. FTIR Spectra of samples modified with 50% of ODTCS and 20% of TMCS at 110°C (45 min).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

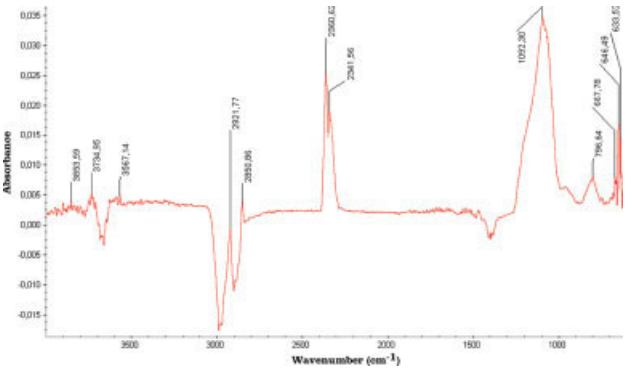

Figure A2. FTIR Spectra of sample modified with 50% of ODTCS and 20% of TMCS at 80°C and 7% RH (45 min).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

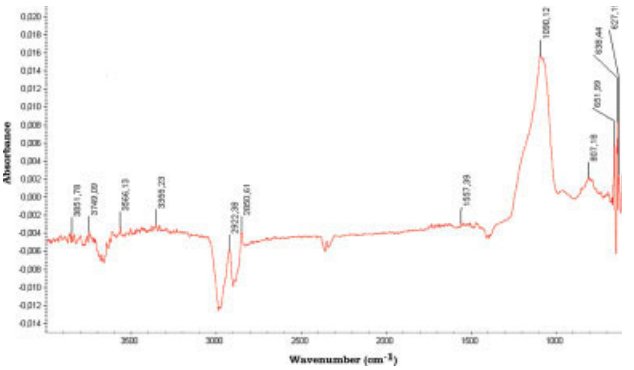

Figure A3. FTIR Spectra of sample modified with 50% of ODTCS and 20% of TMCS at 65°C at 7% RH (45 min).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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