# Preferential grafting of alkoxysilane coupling agents on the hydrophobic portion of the surface of micelle-templated silica

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Silica having a regular mesoporous structure induced by micelle templating (MTS) was functionalised with *n*-propyltrimethoxysilane under anhydrous conditions. Support modification was characterised by various methods (X-ray diffraction, FTIR spectroscopy, thermogravimetry, nitrogen adsorption volumetry, microcalorimetry and FTIR of water adsorption). Functionalisation takes place mainly at the hydrophobic patches of the surface, involving surface siloxane bridges, and occurs through a nucleophilic displacement at the silicon atom by the alkylsiloxane group of the silylating agent. Hydrophilic patches of the surface, consisting of hydrogen-bonded silanol groups, do not constitute, in anhydrous conditions, active sites for the covalent anchorage of the organosilane moieties on the MTS surface.

The chemistry of oxide-immobilised organosilanes is of widespread interest due to extensive applications in chromatography,[1] electrode modification (Pt electrode), enzyme immobilisation,[2] biochemistry,[3] sorption[4] and catalysis.[4–19]

The properties of the grafted solid and the mechanism of silylation are strongly influenced by the state of the surface and the experimental conditions, the main parameters affecting the grafting process being the degree of hydroxylation of the silica surface and the polarity of the solvent used.[20–23] Despite many spectroscopic and chemical investigations, questions remain open about the influence on the functionalisation process of the hydrophilic/hydrophobic behaviour of the surface of a given type of silica.[24–26]

Recently discovered mesoporous micelle-templated silicas (MTS),[27,28] formed by co-operative condensation of amorphous silica around surfactant micelles ordered in regular arrays, may provide more favourable conditions for mechanistic investigations. In a previous paper, the particular hydrophobic and hydrophilic behaviour of the MTS surface has been described.[29] The water–surface interaction has been studied by means of microcalorimetry and IR spectroscopy, and by comparing the results with those for other $H_2O$–$SiO_2$ systems.[30–34] An MTS surface has two distinct portions, showing hydrophobic and hydrophilic properties, respectively. Hydrophobic patches correspond to dehydroxylated portions featuring siloxane bridges and non-interacting silanols. This portion of the surface probably results from a partially irreversible condensation of silanols during the calcination step needed to decompose the surfactant, and is responsible for the overall low silanol content at the MCM-41 surface after calcination: $a_{OH}$ (number of OH groups per nm$^2$) values of 1.2[35] and 2.5–3.0[36] have been proposed. The coexistence of well-defined hydrophilic and hydrophobic patches provides a favourable situation for the study of the silane coupling mechanism.

Grafting of alkoxysilane agents is often performed after activation of the surface by inorganic acids[20] or using catalytic amounts of acidic aqueous solutions in the process to improve grafting *via* a sol–gel process.[21] Such procedures may lead, however, to an island-type grafting due to condensation and clustering of the silylation agents. To avoid this, we carried out the grafting of the outgassed surface in a non-polar solvent, like toluene.[37,38] These reaction conditions favour uniform distributions of grafts, similar to those obtained during controlled vapour deposition.[39]

In the present study, the hydrophobic and hydrophilic behaviour of functionalised MTS has been characterised by microcalorimetry and IR spectroscopy of adsorbed water. Results have been compared with those obtained on the parent silica, with the aim of establishing which type of sites are involved in the surface grafting.

## Experimental

### Materials

The micelle-templated silica was prepared according to a procedure derived from the synthesis of MCM-41.[27] Zeosil 175 MP (Rhône-Poulenc; 42 g, 0.68 mol) precipitated silica was added to a stirred solution of cetyltrimethylammonium (CTMA) bromide (Aldrich; 22 g, 0.068 mol) and sodium hydroxide (6.3 g, 0.16 mol) in deionized water (340 mL) at 343 K. The reagents were heated in a stirred autoclave at 393 K for 16 h. After filtration and successive washing with water and ethanol, the solid phase was dried at 353 K in air, then calcined at 823 K in flowing air for 7 h to eliminate the organic template.

The MTS sample was re-equilibrated with ambient moisture at 298 K for at least 2 days before X-ray measurements. It was then outgassed *in vacuo*: at 473 K (8 h) before $N_2$ sorption experiments and at 423 K before the functionalisation of the surface, the water adsorption and IR measurements.

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**Table 1** Composition of materials determined by elemental analysis and thermogravimetry

| | Calcined MTS | Grafted MTS |
|---|---|---|
| Elemental analysis: %C | <0.02 | 3.44 |
| %N | <0.02 | — |
| %Si | 44.6 | 42.43 |
| Grafting density/nm$^{-2}$ | — | $\leqslant$0.67 |
| $\Delta w(T > 473\ \mathrm{K})$ per $w(\mathrm{SiO_2})$ | 0.014 | 0.052 |
| Grafting density/nm$^{-2}$ | — | $\leqslant$0.77 |

MTS samples functionalised with *n*-propylsilyl groups (referred to hereafter as MTS-2) were prepared by addition of *n*-propyltrimethoxysilane (1.82 g, 13.6 mmol) to a stirred suspension of freshly activated MTS (3 g) in refluxing toluene (50 mL) for 3 h. The toluene solution was monitored for alcohol and ether produced in the degradation of the grafting agent. The solid phase was recovered by filtration, washed in a Soxhlet apparatus using a 1 : 1 diethyl ether and dichloromethane mixture, then dried at 393 K overnight.

**Table 2** Textural characterization by X-ray diffraction and $N_2$ sorption

| | Calcined MTS | Grafted MTS |
|---|---|---|
| $a$/Å | 48 | 48 |
| $S_{\mathrm{BET}}$/m$^2$ g$^{-1}$ | 943 | 896 |
| $S_{\mathrm{BET}}$/m$^2$ g$^{-1}$ of SiO$_2$ | 956 | 943 |
| $C_{\mathrm{BET}}$ | 93 | 68 |
| $V_{\mathrm{mp}}$/cm$^3$ g$^{-1}$ | 0.74 | 0.65 |
| $D$/Å | 40 | 38 |

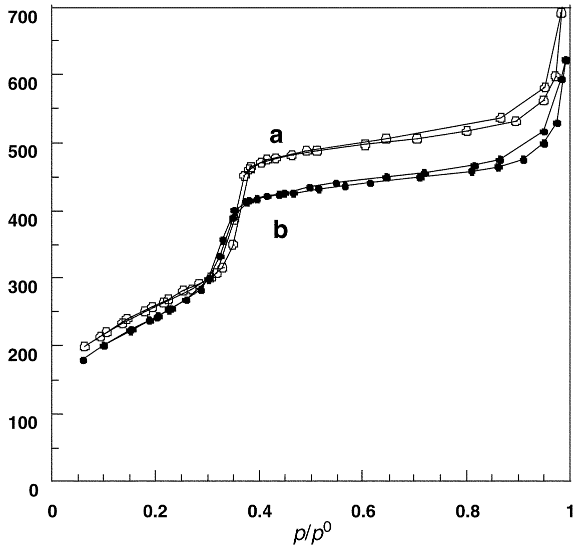


**Fig. 1** $N_2$ adsorption–desorption isotherms at 77 K for micelle-templated silica (*a*) calcined at 823 K and (*b*) functionalised by 0.67 *n*-propylsilyl groups per nm$^2$.

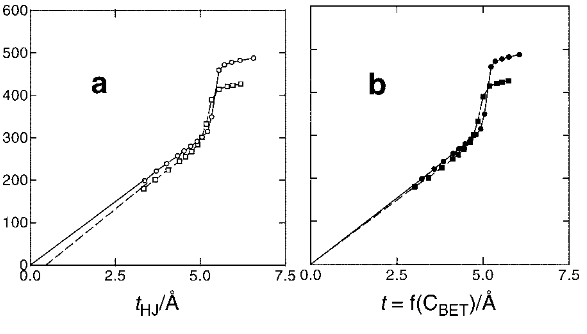


**Fig. 2** Comparison plots (volume adsorbed *vs.* thickness of the adsorbed layer on a non-porous surface) for the isotherms of Fig. 1. (*a*) Standard isotherm of Harkins and Jura. (*b*) Standard isotherms calculated for $C_{\mathrm{BET}} = 93$ and 68, for calcined and grafted MTS, respectively. Circles and solid lines: calcined MTS; squares and dashed lines: grafted MTS.

### Characterisation

Elemental analyses were performed at the Service Central d'Analyses du CNRS in Solaize. Thermogravimetric measurements were carried out on a Setaram SF 85 balance under air flow (25 mg samples heated up to 1123 K at 5 K min$^{-1}$). Powder X-ray diffraction (XRD) patterns were collected using a CGR Thêta-60 diffractometer with monochromated Cu-K$\alpha$ radiation. Textural properties have been determined by $N_2$ sorption at 77 K in a Micromeritics ASAP 2000 apparatus. FTIR spectra of self-supported wafers of samples outgassed at 423 K were recorded on a FT-IR Perkin Elmer 1760-X. Controlled amounts of water vapour were admitted to the sample, and the equilibrium pressure in the IR cell was measured after each dose. Calorimetric and volumetric data were obtained by means of a Tian–Calvet microcalorimeter (Setaram) connected to a volumetric apparatus, allowing simultaneous measurement of the adsorbed amount (uptake, $\eta_a$), heat released ($Q$) and equilibrium pressure ($p$) for small increments of water dose to the solid sample previously outgassed for 2 h at 423 K.[29,33,40] The temperature of the calorimeter was maintained at 303 K throughout the adsorption experiment.

## Results

### Elemental composition

Elemental compositions of the materials are reported in Table 1. The low carbon content of the calcined sample shows that the surface of the parent material is essentially free from organic debris. In the case of the grafted sample, the results of elemental analyses normalized to the surface area of the ungrafted solid allows us to calculate the surface density of grafted chains, by assuming a reasonable model for the graft. Data in Table 1 have been elaborated on the assumption that no alkoxy groups are retained, neither at the graft nor at the surface. In the present case, no information is available on the number of methoxy groups retained, and the estimate of the grafting density, reported in Table 1, has to be considered as an upper limit. Assuming that the density of silanols at the surface of a completely hydroxylated amorphous silica is about 4.6 nm$^{-2}$,[41] the data in Table 1 correspond to a coverage of 0.15 grafted chains per possible surface site.

An alternative evaluation of the number of grafted groups is provided by thermogravimetric (TG) results for the combustion of organics, also reported in Table 1. The organic content is evaluated as the mass loss at temperatures higher than 473 K, and includes some water from dehydroxylation of the surface, as evidenced by the weight loss on the ungrafted sample at $T > 473$ K. Nevertheless, the grafting density calculated from the TG ratio organics/dehydrated silica is in reasonable agreement with the grafting density calculated from elemental analysis. This result suggests that no major loss of grafted groups takes place at temperatures lower than 473 K, and that the outgassing procedure does not alter the characteristics of the samples.

### Textural properties of the samples

The sample of functionalised MTS shows XRD patterns similar to those of the parent all-silica sample, that is the regular mesoporous structure is preserved during the func-

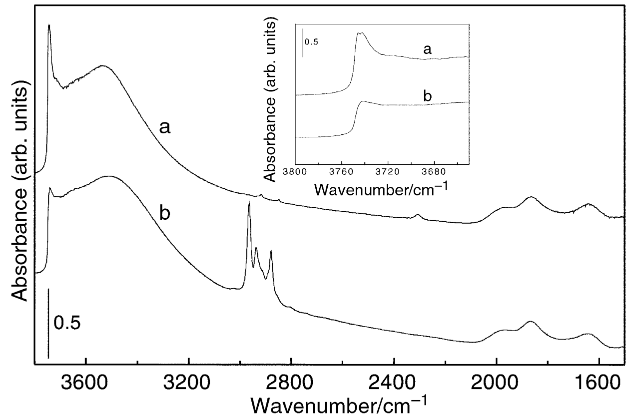
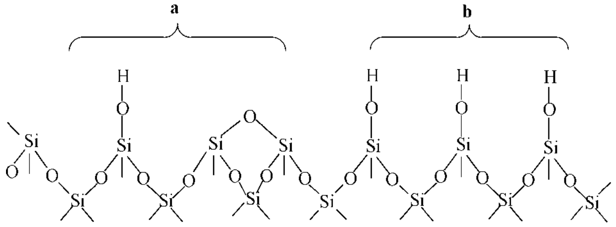


**Fig. 3** Infrared spectra for micelle-templated silica (*a*) calcined at 823 K and (*b*) functionalised by 0.67 *n*-propylsilyl groups per nm$^2$. Wafers outgassed at 423 K.

tionalisation procedure.[22,37] The lattice parameter *a* of the hexagonal array, reported in Table 2, is unaffected by grafting.

$N_2$ sorption isotherms at 77 K for calcined and grafted samples are shown in Fig. 1. They exhibit type IV behaviour, showing a reversible step at $p/p°$ 0.3–0.4, typical of the filling of regular mesoporous systems. Comparison plots of the two isotherms are drawn in Fig. 2(*a*), in which the adsorbed volume is reported *vs.* the *t* function drawn from the standard isotherm of Harkins and Jura.[42,43] The *t*-plot of the calcined sample passes through the origin, confirming the absence of microporosity in the sample. The *t*-plot of the grafted sample crosses the ordinate axis at a negative value, a result with no physical meaning. It is clear that the standard isotherm of Harkins and Jura, reasonably well adapted to the silica surface, provides an inadequate representation of the surface properties of the grafted solid. The treatment of the adsorption data will be discussed in some detail in the discussion section.



**Scheme 1** Schematic representation of surface groups on the (*a*) hydrophobic and (*b*) hydrophilic regions of the surface of calcined micelle-templated silica.

The results of the BET analysis of the portion of the isotherm between 0.05 and 0.20 $p/p°$ are reported in Table 2. The $C_{\mathrm{BET}}$ values for the two samples differ significantly. The value of 93 for the ungrafted sample is a reasonable value for a silica surface calcined at 550 °C and largely rehydroxylated. The lower value observed for the grafted sample ($C_{\mathrm{BET}} = 68$) corresponds to the average value expected for a silica surface partially functionalised by organic groups.[44]

Mesoporous volumes $V_{\mathrm{mp}}$, measured at the top of the mesopore-filling step of the isotherm, are also reported in Table 2. The evaluation of pore size in ordered mesoporous materials has raised some debate. Pore diameters *D* reported in Table 2 have been calculated from the lattice parameter *a* and the void fraction of the hexagonal pore pattern.[45] The void fraction has been calculated from the mesoporous volume, assuming densities of 2.2 and 0.8 g cm$^{-3}$ for the silica walls and the organic coating, respectively. Mesoporous volumes, surface areas and pore diameters of the functionalised sample are lower than the corresponding values for the parent MTS, as expected if the mineral walls are lined with grafting agents.

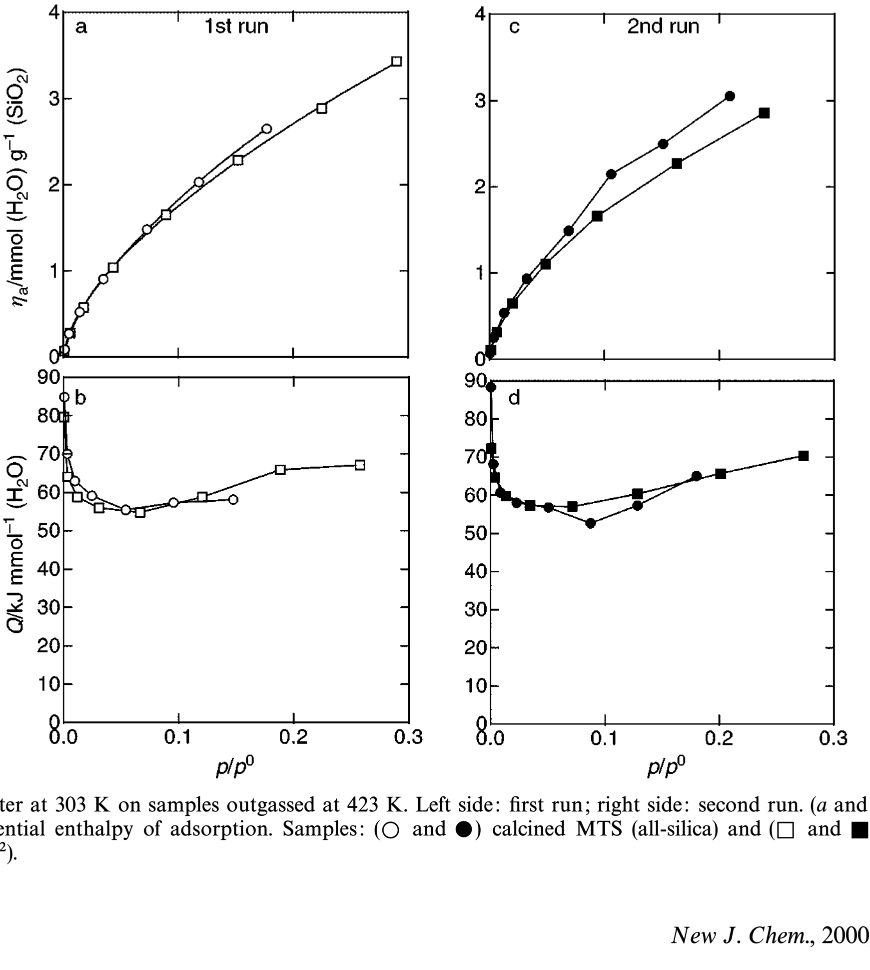


**Fig. 4** Adsorption of water at 303 K on samples outgassed at 423 K. Left side: first run; right side: second run. (*a* and *c*) Adsorbed amount $n_a$ *vs.* $p/p°$. (*b* and *d*) Differential enthalpy of adsorption. Samples: (○ and ●) calcined MTS (all-silica) and (☐ and ■) grafted MTS (0.67 *n*-propylsilyl groups per nm$^2$).

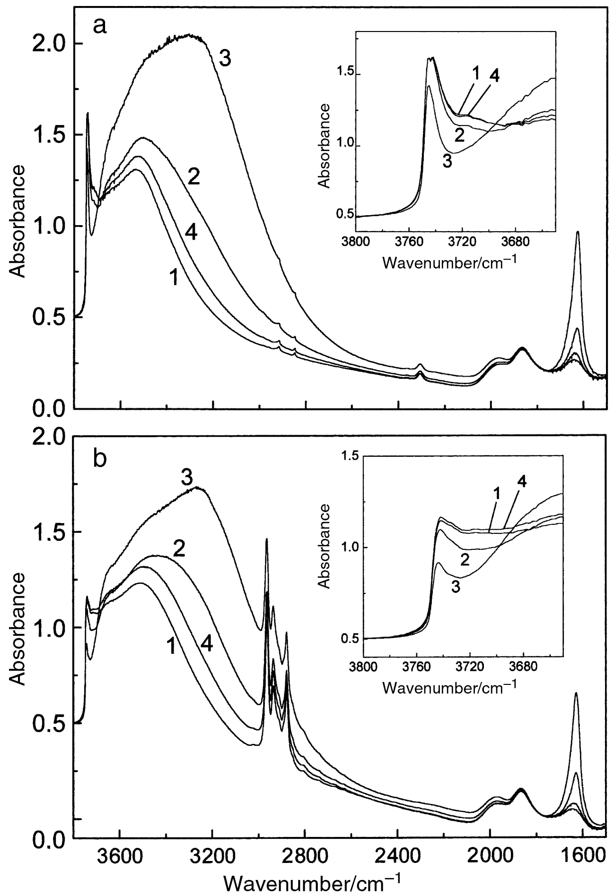


**Fig. 5** Infrared spectra of water dosing on (*a*) calcined MTS (all-silica) and (*b*) grafted MTS (0.67 *n*-propylsilyl groups per nm$^2$). Curve 1: wafer outgassed at 423 K; curve 2: after adsorption at 1.35 Torr; curve 3: after adsorption at 9 Torr; curve 4: evacuated at room temperature after adsorption.

### FTIR characterisation

Infrared spectra of the samples outgassed at 473 K are presented in Fig. 3. To highlight the frequency range characteristic of the free and terminal silanols, the portions of the spectra in the 3650–3800 cm$^{-1}$ range are shown at higher magnification in the insets. The curve for the grafted sample shows a sharp double band with maxima at 3747 and 3742 cm$^{-1}$ and a weaker band at 3715 cm$^{-1}$, due to isolated hydroxyl groups, and a broad envelope centred at about 3536 cm$^{-1}$, with a tailing towards lower frequencies and a shoulder at about 3653 cm$^{-1}$. The band pair at 3715 and 3536 cm$^{-1}$ is assigned to clustered, H-bonded silanols constituting the hydrophilic sites.[29] The component at 3715 cm$^{-1}$ is due to the stretching mode of the terminal silanol, and the component at 3536 cm$^{-1}$ to the H-bonded partner. A simplified model of the surface groups is given in Scheme 1. Note that other authors observed only one band due to isolated hydroxyls at 3738 cm$^{-1}$.[36] The band at 3742 cm$^{-1}$ appears to be related to a quasi-free species, typical of hydrated surfaces.

Grafting of less than one *n*-propylsilyl group per nm$^2$ corresponds to a marked decrease of the intensity of the bands at 3747 and 3742 cm$^{-1}$ (isolated silanols), whereas the bands due to bonded silanols are little affected, both at 3715 (terminal species) and at 3536 cm$^{-1}$ (H-bonded partner). Grafting seems to affect the hydrophobic portion of the surface of MTS (isolated silanols) more than the hydrophilic portion (interacting silanols). CH modes are logically present in the spectrum of the grafted sample: two bands at 2936 and 2867 cm$^{-1}$ are assigned to the asymmetric and symmetric vibrations, respectively, of $CH_2$ groups in the propyl chain, and the most intense band at 2966 cm$^{-1}$ is assigned to the asymmetric $CH_3$ deformation. The corresponding symmetric mode probably overlaps with the 2867 cm$^{-1}$ band. Methyl groups occur either as terminal groups in the *n*-propyl chains or as methoxy groups. The latter may, in turn, either be present at the graft or be bound at the silica surface by reaction with a surface silanol.

### Water adsorption isotherms and calorimetric data

The isotherms of adsorption of water vapour on ungrafted and grafted samples outgassed at 423 K (first runs) are reported in Fig. 4(*a*). The amount adsorbed is expressed in mmol per gram of silica, in order to refer all data to the same amount of ungrafted surface. The amount of water adsorbed at a given pressure is slightly smaller in the case of the grafted sample. The decrease of adsorption with grafting is less than proportional to the corresponding decrease in surface area, as measured by $N_2$ adsorption at 77 K.

Differential heats of water adsorption as a function of relative pressure are reported in Fig. 4(*b*). Data for the ungrafted sample have already been published.[29] The high initial heat of adsorption for the first dose corresponds to a limited number of highly hydrophilic sites. The plateau at 55–60 kJ mol$^{-1}$ in the $p/p^\circ$ range *ca.* 0.02–0.12, unaffected by grafting, suggests that water is adsorbed on a similar hydrophilic surface on both samples, notwithstanding the presence of grafts. The increase in adsorption heat at relative pressures higher than *ca.* 0.12 corresponds to collective phenomena depending on the curvature of the pore surface.[29]

The results of the second adsorption runs, after intermediate outgassing at 303 K, are reported in Fig. 4(*c*,*d*). The volumetric isotherms $\eta_a$ *vs.* $p/p^\circ$ [Fig. 4(*c*)] for ungrafted and grafted MTS are very similar to the results of the first runs. Differential enthalpies measured in the second runs are reported in Fig. 4(*d*) as a function of $p/p^\circ$. The plateau at 55–60 kJ mol$^{-1}$ in the $p/p^\circ$ range 0.02–0.15 is present in the second as well in the first run for both samples. At higher pressures, cooperative phenomena raise somewhat the heat of adsorption.

### IR spectroscopy of water adsorption

Fig. 5 presents the IR spectra obtained by dosing water on the ungrafted [Fig. 5(*a*)] and grafted [Fig. 5(*b*)] MTS samples. Spectra are reported for samples outgassed at 423 K (curve 1), equilibrated with water at 1.35 (curve 2) and 9 (curve 3) Torr and outgassed again at room temperature (curve 4). Basically the same phenomena are observed for both samples. The band at 3747 cm$^{-1}$ due to isolated silanols[29] is not involved in the water adsorption (curves 2 and 3). The interaction with water concerns the components lying at slightly lower frequencies (3742 and 3715 cm$^{-1}$), corresponding, respectively, to geminal and terminal species in H-bonded silanols[46] (Scheme 1). The increasing absorption in the 3600–2700 cm$^{-1}$ region corresponds to vibrations of water aggregates. The band at 1628 cm$^{-1}$ (bending mode of molecular water) significantly increases with water pressure. After evacuation at room temperature (curve 4), the spectra nearly coincide with the initial ones (curve 1), in agreement with the reversibility of water adsorption deduced from the calorimetric data.

## Discussion

The results of $N_2$ adsorption at 77 K and X-ray diffraction (Table 2) indicate that the regular mesoporous structure of the support is preserved during the silylation procedure, as expected considering that the anhydrous and apolar medium used (toluene) prevents solvolysis of the inorganic support.

Surface area and mesoporous volume decrease as a result of the lining of mesopores by organic chains.[22,37]

The efficiency of the functionalisation is witnessed by the decrease of the parameter $C_{BET}$ from the ungrafted to the grafted sample. The parameter $C_{BET}$ is related to the excess enthalpy of condensation of the nitrogen molecules of the first monolayer adsorbed $\{C_{BET} = \exp[(\Delta H_{ads} - \Delta H_L)/RT]$, where $\Delta H_{ads}$ is the enthalpy of condensation of a molecule in the monolayer and $\Delta H_L$ is the enthalpy of condensation to the bulk liquid phase$\}$. The coverage of a silica surface by organic molecules decreases the enthalpy of adsorption of nitrogen, and $C_{BET}$ values can decrease from nearly 100 for a hydroxylated silica surface to 15 for a completely silylated surface.[44] The BET treatment has been derived with the hypothesis of a surface which is homogeneous with respect to nitrogen adsorption. In the present case, however, the nitrogen molecule interacts with two different types of surfaces (oxide and hydrocarbon) and the measured $C_{BET}$ value corresponds to an average interaction.

The $C_{BET}$ parameter expresses the strength of the adsorbate–adsorbent interaction and characterizes the shape of the adsorption isotherm for a given nature of the surface. The proper standard isotherm for each type of surface can be calculated from the $C_{BET}$ value by the *n*-method of Lecloux and Pirard.[47] Standard isotherms determined for the $C_{BET}$ value of each sample (93 for the ungrafted and 68 for the grafted sample) have been used to draw the comparison plots in Fig. 2(*b*). Both plots pass through the origin, indicating that the difference in the $C_{BET}$ values is significant and that no microporosity has been created by the grafting process.

Notwithstanding the presence of two different kinds of surfaces, the calorimetry of water adsorption shows that enthalpic and volumetric data are very similar for grafted and ungrafted sample. Previous microcalorimetric and IR studies of water adsorption on ungrafted MTS have shown the peculiar behaviour of micelle-templated silicas:[29] (*i*) low amounts of water are adsorbed (close to the values measured on pyrogenic silicas), due to the presence of hydrophobic portions of the surface formed from siloxane bridges and isolated silanols; (*ii*) differential heat shows a plateau at about 60 kJ mol$^{-1}$ (a value higher than that for most hydrophilic silicas) over a wide pressure range (0.03–0.2 $p/p°$). This plateau is attributed to the adsorption of water on H-bonded chains of interacting silanols, constituting the hydrophilic portion of the surface; (*iii*) adsorption heat increases beyond $p/p°$ 0.2, due to co-operative effects related to the formation of water clusters favoured by the curvature of the surface. All these features are still present in the grafted samples. Water uptakes are of the same order of magnitude on the ungrafted and grafted samples, and differences between them roughly follow the trend of surface area, which decreases with organic coverage. First and second adsorption runs are very close to one another for ungrafted and grafted samples. The adsorption of water takes place at essentially the same enthalpy for both samples, which present a plateau at an enthalpy level of 55–60 kJ mol$^{-1}$.

Calorimetric data and adsorption isotherms are coherent with a model in which the nature of the hydrophilic portion of the surface is essentially unaffected by the grafting process. The extent to which silylation affects the area of the hydrophilic surface can be evaluated by further analysis of the water adsorption isotherms. Useful comparison among water isotherms can be obtained by application of the BET treatment, notwithstanding the localised nature of the water adsorption.[48] The results of the BET treatment of the water isotherms of Fig. 4(*a*) are reported in Table 3. It can be observed that the monolayer coverage of water decreases with grafting with a trend roughly proportional to the decrease of surface area, as evaluated by $N_2$ adsorption and reported in Table 2. A more precise comparison provides an evaluation of the fraction of surface available for the adsorption of water. The monolayer coverage of water on the surface of the ungrafted sample is 2.02 molecules nm$^{-2}$ (Table 3). Under the assumption that this value remains constant on the ungrafted portion of the surface, the decrease of the monolayer coverage with grafting is proportional to the fraction of hydrophilic surface coated with organics. This evaluation of the fraction of grafted surface is reported in the third row of Table 3. No more than 15% of the hydrophilic surface has been made hydrophobic by grafting. This value can be compared to the grafted area as evaluated by independent methods and able to take into account both the hydrophilic and hydrophobic portions of the surface. Under the assumption that the $C_{BET}$ values for the adsorption of $N_2$ are average values between portions of the surface at $C_{BET}$ values of 93 (ungrafted MTS) and 15 (silylated surface,[44] the fraction of grafted surface can be evaluated from the $C_{BET}$ value reported in Table 2. The elemental analysis of grafted sample provides another estimation of the grafted area. If it is assumed that the average silyl group is bonded to the surface by two Si–O–Si bonds and that theoretically complete functionalisation of the surface corresponds to 4.6 bonds nm$^{-2}$ (silanol density of a completely hydroxylated amorphous silica),[41] the surface density of grafted groups reported in Table 1 gives another evaluation of the fraction of grafted surface. The results of all methods of evaluation of the grafted area are reported in Table 3, and it appears clearly that the hydrophilic portion of the surface has been affected by grafting less than proportionally (area decrease as evaluated by BET $H_2O \ll C_{BET}\ N_2 \sim$ graft analysis).

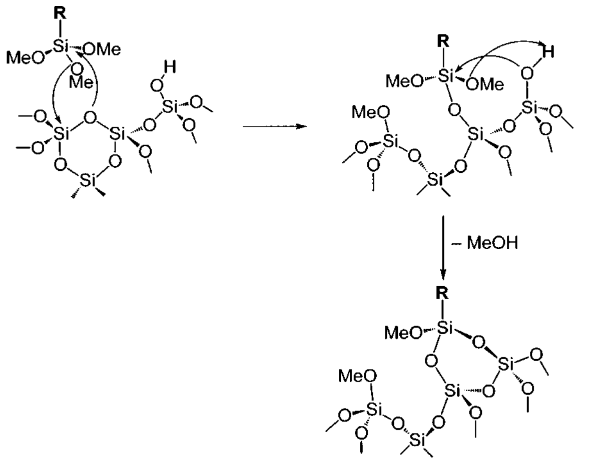
**Table 3** BET analysis of the water adsorption isotherms and evaluation of the fraction of grafted surface by different methods

| | Calcined MTS | Grafted MTS |
|---|---|---|
| $\eta_a(H_2O)$/mmol g$^{-1}$ of $SiO_2$ | 3.22 | 2.74 |
| $\eta_a(H_2O)$/molecules nm$^{-2}$ | 2.02 | 1.75 |
| Fraction of grafted surface: | | |
| BET $H_2O$ | 0.00 | 0.14 |
| $C_{BET}$ $N_2$ | 0.00 | 0.30 |
| Graft anal. | 0.00 | 0.29 |

The observation that silylation reduces the hydrophilic portion of the surface less than expected is coherent with the spectroscopic data. The evolution of the IR spectra during the adsorption of water confirms that water interacts mainly with the H-bonded silanols, which are preserved during the modification of the surface, as grafting at the MTS surface takes place basically on the hydrophobic part. This indicates that the free silanols are engaged in the silylation process as suggested by the decrease of the isolated silanol band of the modified MTS spectra. A fraction of siloxane bridges is liable to anchor organosilane chains. This assumption is supported by previous data independently obtained during the silylation process of silica by Dubois and Zegarski[25] and by Blümel.[26] The former used methyltrimethoxysilane as the coupling agent in gas phase and *in situ* IR measurements, the latter used trimethylethoxysilane in toluene solution and $^{13}C$ MAS NMR measurements of the resulting solids. The mechanism suggested by these authors implies siloxane bridges through a nucleophilic attack at the silicon atom, according to the equation:

$$[SiO_3]O[SiO_3] + CH_3Si(OCH_3)_3 \rightarrow CH_3(CH_3O)_2SiO[SiO_3][SiO_3]OCH_3$$

In agreement with such views, and taking into account the absence of noticeable reaction involving H-bonded silanol



**Scheme 2** Schematic representation of the mechanism of silylation.

groups, the coupling mechanism probably consists of combined nucleophilic substitutions at the silicon atoms of both surface siloxane and silylating agent, which are pictured in Scheme 2.

Taking into account that the electron donor ability of oxygen decreases in the order C–O–C > C–O–Si ≫ Si–O–Si,[49,50] nucleophilic attack by the oxygen of the surface siloxane would be negligible with respect to that involving the alkoxysilane group. Nevertheless, the electron donor ability of strained surface siloxane bridges is known to be higher than that of the unstrained ideal bridges $(CH_3)_3Si–O–Si(CH_3)_3$. Moreover, involvement of such a nucleophilic attack would be favoured through bonding electron delocalisation induced by the concerted nucleophilic attack of a silicon atom of the siloxane group by the oxygen of the methoxy group.

In order to explain the decrease in the free silanol content, we assume that the anchoring process involves a neighbouring free silanol, in accordance with alcohol formation during the silylation process. It is very likely that in the presence of water the silylation pathway is completely different. A silica surface in contact with water presents, at most pH values, a significant amount of deprotonated silanols. In the presence of such an efficient nucleophilic agent, the silane undergoes a nucleophilic attack. As a consequence, the mechanism of silylation in the presence of water is electrophilic, rather than nucleophilic, and grafting from aqueous solution takes place mainly on the hydrophilic portion of the silica surface.[51–53] The possibility of such a reaction has also been discredited by $^{29}Si$ and $^{13}C$ MAS-NMR studies that some of us have recently published.[54]

## Conclusions

The functionalisation of MTS using alkoxysilane coupling agents in apolar solvent takes place mainly on the hydrophobic portion of the surface with the hydrophilic portion, consisting of hydrogen-bonded silanol groups, being preserved. These silanol groups are not the active sites for the covalent anchorage of the organosilane moieties onto the MTS surface under anhydrous conditions, in contrast with some recent assumptions.[51,52,55] The mechanism of the surface functionalisation involves surface siloxanes and free silanols and the alkylsiloxane of the silylating agent through nucleophilic displacement at the silicon atom without alteration of the hexagonal mesoporous structure of the mineral support.

The modification of silica by grafting of organic chains is currently used to prepare hybrid materials with catalytical functions. The properties of the catalytic site can be affected by its hydrophilic or hydrophobic environment.[22] In this respect, the evidence for the persistence of hydrophilic areas on surfaces partially grafted in hydrophobic conditions can be relevant for the choice of the surface treatments aimed to improve catalytic activity and selectivity.

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