PAPER www.rsc.org/njc | New Journal of Chemistry

Characterisation of the grafting of (3-aminoethyl)aminopropyltrimethoxysilane on precipitated silica

Sophie de Monredon,[a] Agnès Pottier,[b] Jocelyne Maquet,[a] Florence Babonneau*[a] and Clément Sanchez[a]

Received (in Montpellier, France) 16th December 2005, Accepted 3rd March 2006
First published as an Advance Article on the web 30th March 2006
DOI: 10.1039/b517934c

In this study, we have investigated the reaction between (3-aminoethyl)aminopropyltrimethoxysilane (AEPTS) and a precipitated silica in organic solvents. Solid-state ^{29}Si NMR and Karl Fischer titration have been used to produce useful information on the grafted silica samples. AEPTS was chosen in order to characterise the distribution of alkoxysilanes at the silica surface. Indeed, this alkoxysilane has an ethylene diamine function that can form coloured and paramagnetic complexes with copper in 1 : 1 and 2 : 1 molar ratios ($[\mathrm{Cu(AEP\text{-}Si{\equiv})}]^{2+}$ and $[\mathrm{Cu(AEP\text{-}Si{\equiv})_2}]^{2+}$). These species have been further identified and quantified by UV-visible and ESR spectroscopies, and the proximity of the alkoxysilanes at the surface was thus traced back through the detection of the 2 : 1 complex $[\mathrm{Cu(AEP\text{-}Si)_2}]^{2+}$.

Introduction

The surface modification of silica particles by silylation has a large impact in various and important areas of chemistry such as chromatography,[1,2] optics,[3] catalysis and biochemistry.[4–6] Although a wide variety of alkoxysilanes can react with surface silanol groups, the structural control of the surface coverage is still an important subject of research. Indeed, alkoxysilanes, and particularly trialkoxysilanes, are most often used to modify the silica surface. They are usually monomeric species with the general formula $\mathrm{RSi(OR')_3}$, where R is a functional group. In organic medium, water of hydratation of the silica particles can serve as a hydrolysis source for the alkoxy groups of the alkoxysilanes. Then after hydrolysis, the alkoxysilanes can condense, either with the surface silanols, to produce a monolayer coverage *via* a siloxane anchoring or with itself leading to a polysiloxane network on the nanoparticle surface. Because of the very low concentrations of grafted molecules in the samples, very few studies of chemically modified silica particles deal with the quantification of the particle coverage.

After surface modification, these alkoxysilanes can themselves be further modified, providing the ability to tailor surfaces for specific purposes. For example, alkoxysilanes such as (3-aminoethyl)amino-propyltrimethoxysilane (AEPTS) with an ethylenediamine function, have been used on siliceous surfaces to preconcentrate metal ions for multielement determination by X-ray spectrometry.[7] In the present study, the complexation property of AEPTS has been exploited to elucidate the distribution of grafted functions as well as their proximity on the silica surface.[8–10] To reach this objective, the surface silanol groups have been first quantified by Karl Fischer titration to estimate the amount of alkoxysilanes needed to form a monolayer. Then, the AEPTS grafted particles have been characterised by ^{29}Si solid-state NMR. Finally, chemical analysis and UV-visible and ESR spectroscopies have been combined to evaluate the complexing ability of the grafted functions *versus* $\mathrm{Cu^{2+}}$ ions, which will allow a discussion about the spatial distribution of the functions on the surface.

Experimental

Synthesis

Grafting of silica by AEPTS. The precipitated silica was provided by Rhodia (Aubervilliers, France). It is characterised by a BET surface area of 160 $\mathrm{m^2\ g^{-1}}$ and a water content of 5 wt%. The silica powder (2 g, 10 wt%) was first dispersed in anhydrous toluene (20 g). Then a given amount of the AEPTS (Aldrich, Table 1) was added and the reaction mixture was stirred at ambient temperature for 2 hours. The modified silica particles were then recovered after centrifugation and washed with ethanol. In order to eliminate the residual free or adsorbed alkoxysilanes species, derived from AEPTS, a Soxhlet extraction was performed in $\mathrm{Et_2O/CH_2Cl_2}$ (50/50 v/v) mixture under reflux during 4 hours. The particles were then dried under vacuum.

Complexation with $\mathbf{CuCl_2}$. An alcoholic (20 mL of methanol) suspension of modified silica particles (50 mg) was reacted with an excess of anhydrous $\mathrm{CuCl_2}$; the particles turned blue immediately. They were filtered off from the solution, then washed with ethanol and dried under vacuum at room temperature.

Characterisation techniques

Elemental analysis was carried out at the "Centre d'analyses du CNRS" (Vernaison, France) in order to determine the

---

[a] *Laboratoire de Chimie de la Matière Condensée de Paris CNRS UMR 7574, Université Pierre & Marie Curie, 4 place Jussieu, 75252 Paris Cedex 5, France. E-mail: fb@ccr.jussieu.fr*
[b] *Rhodia Recherches, 52 rue de la Haie Coq, 93308 Aubervilliers, France*

quantity of AEPTS grafted onto the silica, from the N/Si molar ratio.

A Karl Fischer titration was performed to quantify the amount of water and silanol groups at the surface of particles.[11] Usually the titration is a direct measurement of the water content, through reaction (1):

$$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI \qquad (1)$$

But, when methanol is used as solvent, a secondary reaction occurs between MeOH and the silanol groups which produces a stoichiometric amount of water according to reaction (2):

$$\text{MeOH} + \text{Si–OH} \rightarrow H_2O + \text{Si–OMe} \qquad (2)$$

The number of silanols can thus be obtained by difference from the two titration reactions. Titration with Karl Fischer Reagent 5 (KFR 5: provided by Hydranal) in methanol (reaction (2)) allows the determination of the number of silanols and water molecules, while the measurement leads only to the amount of water adsorbed onto silica if another reagent KFR 5K from Hydranal and another titration solvent (chloro-2-ethanol/chloroform mixture designed as "arbeitsmedium solvent" by Hydranal) are used. Each titration was reproduced three times with 200 mg of powder in about 150 mL of solvent. To measure the water and silanol contents simultaneously, an extraction time of 10 min, was used to be sure that the transalcoholysis reaction (2) was completed.

The NMR experiments were performed on a spectrometer (Bruker MSL 300) operating at 300.13 MHz for ^1H and 59.62 MHz for ^{29}Si equipped with a 7 mm Bruker MAS probe spinning at 4 KHz. ^{29}Si MAS NMR spectra were recorded with a pulse width of 6 μs (*ca.* 90°) and a recycling delay of 5 min. This value was chosen after T_1 measurements in order to obtain quantitative data. The ^{29}Si CP-MAS NMR spectra were recorded with a 90° pulse of 6 μs, a contact time of 5 ms and a recycling delay of 5 s. 15 000 transients were acquired. ^{29}Si isotropic chemical shifts are referenced to TMS ($\delta = 0$ ppm). The accuracy of the chemical shift is ±0.3 ppm. The spectra were simulated with the DmFit software.[12]

UV-visible spectra were recorded on a spectrometer Uvikon 940 from 300 to 900 nm. 50 mg of AEPTS-grafted silica treated with $CuCl_2$ were suspended in 4 mL of water; the suspension was stable during the time needed for the measurement. Blank experiments were performed with a dispersion of AEPTS-grafted silica in water under the same conditions. ESR experiments were performed at 77 K on a Varian CST 104 spectrometer, operating at 9.3 GHz (X-band).

Results and discussion

Quantification of the surface silanol groups

Characterisation of the silica surface chemistry in terms of water and silanols has been largely studied.[13–17] However, the large range of silica powder samples, with their corresponding differences in surface properties makes comparison difficult regarding the efficiency of the grafting reactions. The number of accessible silanols present at the surface has to be known accurately, since each one of them represents a potential grafting site. Several methods have been reported to quantitatively evaluate the silanol sites. Theoretical calculations,[18,19] infrared,[13] thermogravimetric analysis[20] (TGA), ^{29}Si NMR[13,14,20] or deuteration[21,22] are the most often used. In the present study, a not so widely used technique, Karl Fischer titration,[23] was tested and provided rapid and accurate information.[24] It was performed on silica particles before surface modification following the procedure described in the Experimental section. 5.5 wt% H_2O was found in agreement with Rhodia's specifications and thermogravimetric measurements (not presented here). As for the silanol content, a quantity of 3.5 OH nm^{-2} was found, using for the BET surface area a value of 160 $m^2\ g^{-1}$. Assuming that each of these OH can be a potential grafting site, then conversion of all $\equiv$SiOH groups into $\equiv SiOSi(CH_2)_3NH(CH_2)_2NH_2$ groups, which lead to a monolayer coverage, corresponds to 20 wt% of AEPTS.

Characterisation of the grafting

The composition of the different samples are reported in Table 1. From the N and C contents obtained from elemental analysis, the amount of alkoxysilanes which have reacted with the surface can be calculated (Table 1). Values greater than 83% of the initial AEPTS were found, except when the quantity introduced corresponded to more than a monolayer coverage (sample A). This suggests that grafting occurs probably without any extensive polycondensation of the alkoxysilanes, that could have occurred in the organic solvent. The

Table 1 Composition of samples extracted from chemical analysis and UV-visible absorption data

Sample	Initial AEPTS : SiO_2/ wt%	Amount of AEPTS grafted[abc]/ wt%	Grafting yield (%)	N^d/wt%	Cu^d/ wt%	N : Cu/ mol%	$[Cu(AEP\text{-}Si)_2]^{2+}$ (%)	$[Cu(AEP\text{-}Si)]^{2+}$ (%)	[*C*]/μmol m^{-2}	*r*/Å $molecule^{-1}$
A	50	22	44	—	—	—	70	30	—	—
B	20	17	85	2.10	2.35	4.0	70	30	6	5.2
C	10	8.5	85	1.16	1.61	3.3	80	20	3	7.5
D	5	4.5	90	0.74	1.04	3.2	35	65	1.5	10.5
E	4	3.5	88	0.42	0.70	2.7	—	—	—	—
F	3	2.5	83	0.36	0.69	2.4	30	70	—	—
G	2	2	100	0.26	0.45	2.6	25	75	0.6	16.5
H	1	> 1.2	—	0.12	0.20	2.7	—	—	0.3	23.5
I	0.5	> 0.6	—	< 0.09	0.15	< 2.7	—	—	0.15	33.3

[a] From chemical analysis. [b] Calculation takes into account the water content after synthesis. [c] Accuracy: ±10%. [d] From chemical analysis after complexation.

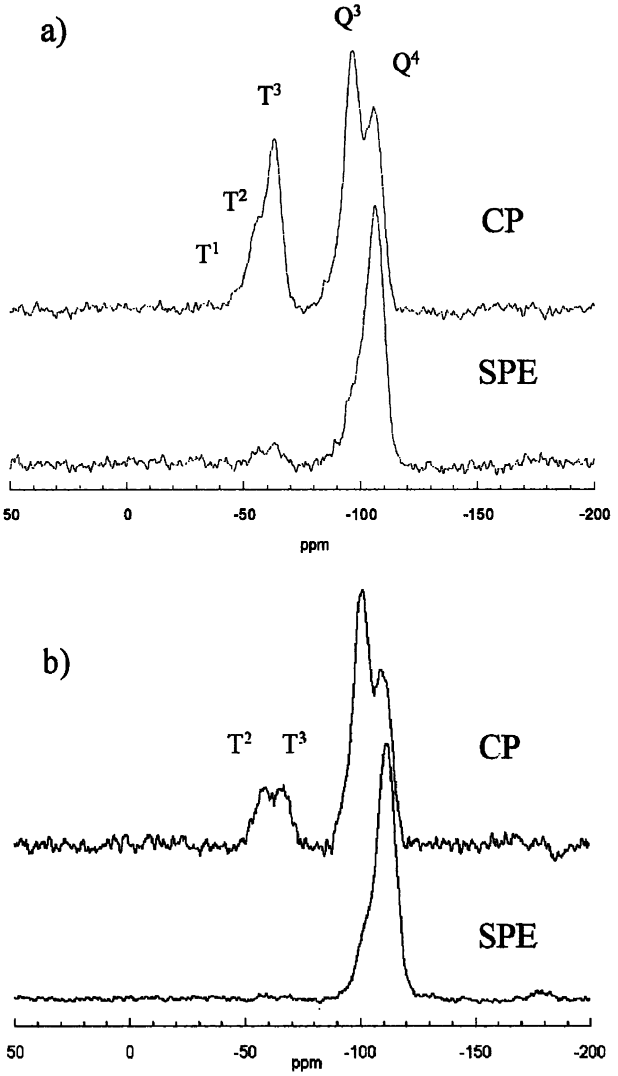

Fig. 1 ^{29}Si MAS and CP-MAS NMR spectra of a) sample B ($AEPTS/SiO_2$ = 20 wt%) and b) sample C ($AEPTS/SiO_2$ = 10 wt%).

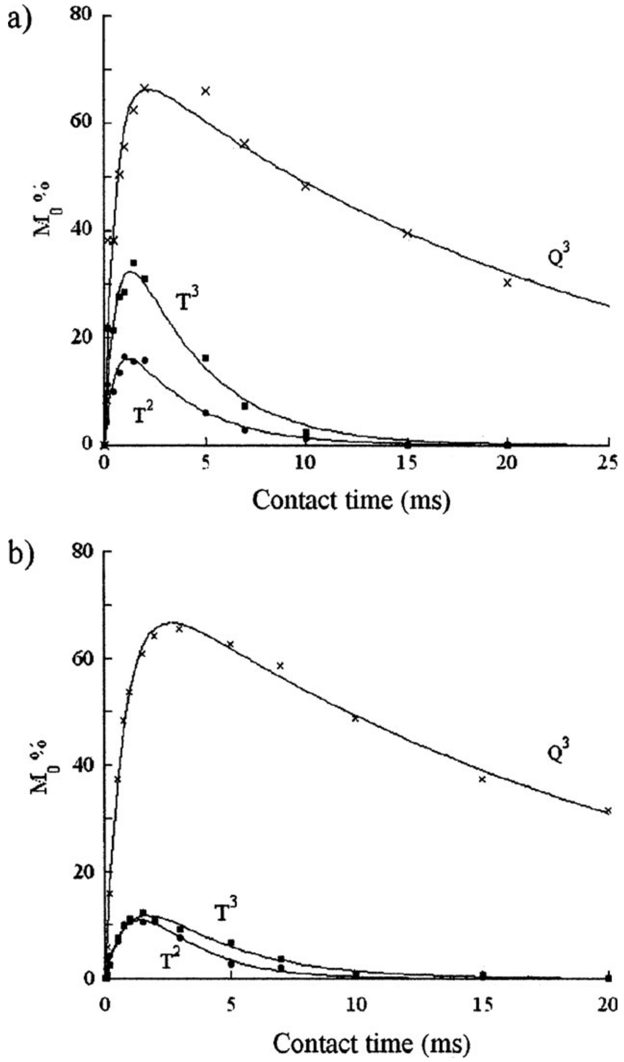

Fig. 2 Plots of NMR line intensity as a function of contact time for ● T^2, ■ T^3 and × Q^3 units of a) sample B (initial $AEPTS/SiO_2$ = 20%) and b) sample C (initial $AEPTS/SiO_2$ = 10%).

maximum coverage is indeed reached, as expected, for an initial 20 wt% of AEPTS.

Fig. 1 presents the ^{29}Si MAS NMR spectra of samples B and C recorded through a single pulse experiment (SPE) or a ^{1}H–^{29}Si cross polarization experiment (CP). The resonance peaks at −102 and −111 ppm are assigned respectively to the Q^3 and Q^4 units of the silica particles. The resonances at −51, −59 and −67 ppm correspond to the T^1, T^2 and T^3 units of the aminosilane in interaction with the surface. These signals are intense in the CP-MAS spectra, but barely detectable in a SPE-MAS experiment even for an initial quantity of AEPTS ≥ 20 wt%. A simulation of the spectrum gives the following molar ratios: $T^2/T^3/Q^2/Q^3/Q^4$ = 2.6 : 3.9 : 2.0 : 22.5 : 69.0 (T/Q = 0.07), which corresponds to a N/Si molar ratio of 0.13, in excellent agreement with the elemental analysis result N/Si = 0.139. The SPE-MAS experiment thus provides direct quantification of the different surface units for sample B, but not for sample C, because of a too low concentration of grafted molecules. For such samples, it would be very useful to try to quantify the various Si sites from the ^{29}Si CP-MAS NMR spectrum.

Unlike the SPE-MAS experiment, the CP-MAS experiment is not inherently quantitative. Intensities in the CP-MAS spectrum reflect local cross-polarization dynamics which may vary from site to site. In order to obtain semi-quantitative data by CP-MAS experiment, we acquired polarization measurements with variable contact times. Fig. 2 gives the corresponding plot of the measured NMR signal intensities as a function of contact time.

These curves can be fitted with eqn (3),

$$M(t_c) = \frac{\gamma_H}{\gamma_{Si}} M_0 \frac{1}{1-\lambda}\left[1-\exp\left(-\frac{(1-\lambda)t_c}{T_{\mathrm{SiH}}}\right)\right]\exp\left(-\frac{t_c}{T_{1\rho}}\right)$$

$$\lambda = \frac{T_{\mathrm{SiH}}}{T_{1\rho}} \qquad (3)$$

which describes the dynamics of magnetization transfer *versus* contact time between a proton spin reservoir and the ^{29}Si dilute spins.[25] T_{SiH} represents the CP standard time that is related to the strength of the ^{1}H–^{29}Si dipolar coupling. $T_{1\rho}$ is the relaxation time of the abundant ^{1}H spins in the rotating frame and M_0 is the magnetization of the system at equilibrium in the static field B_0. M_0 is thus directly proportional to the number of ^{29}Si spins detected by the CP experiment. Because of the lack of protons in the local environment of a large number of the Q^4 units, the associated signal is largely underestimated and will not be considered. For the signals due to the T^2, T^3 and Q^3 units, one can reasonably assume that all of the units are detected because of the presence of protons in their close proximity. The three corresponding curves have thus been fitted according to eqn (3) (Fig. 2a). $T_{1\rho}$ was previously measured independently to constrain the fitting procedure: a value of 2 ms was found for the various units in agreement with the assumption of a unique proton bath. The relative intensities, $T^2/T^3/Q^3 = 8.4 : 13.9 : 77.7$, are in good agreement with the values found from the SPE spectrum ($T^2/T^3/Q^3 = 9.0 : 13.4 : 77.6$).

This study on sample B shows that the $T^2/T^3/Q^3$ relative intensities can be directly quantified from the analysis of the CP response at various contact times; since the Q^3/Q^4 ratio can be extracted from the SPE spectrum, combination of both SPE and CP experiments allows the estimation of the T/Q molar ratios, and thus the amount of grafted alkoxysilanes, even when the T units cannot be detected in the SPE spectrum. This approach was applied for sample C. Fits of the CP curves (Fig. 2b) lead to the following quantification: $T^2/T^3/Q^3 = 7.6 : 6.8 : 85.6$. The Q^3/Q^4 ratio extracted from the SPE spectrum (Fig. 1) gave 18.3 : 81.7. Combining both results leads to the following quantification $T^2/T^3/Q^3/Q^4 = 1.6 : 1.4 : 17.7 : 79.3$, thus T/Q = 3%. This value is in excellent agreement with the elemental analysis results (N/Si molar ratio = 0.06). This study demonstrates the possibility of quantifying the amount of grafted alkoxysilanes even for low concentrations by combining the ^{29}Si SPE and CP-MAS NMR results.

Distribution of AEPTS on the silica surface

AEPTS was chosen in order to characterise the distribution of the grafted species on the silica surface. Upon addition of copper(II) chloride to an alcoholic suspension of AEPTS modified silica, very stable 1 : 1 and 2 : 1 complexes may be obtained ($[\mathrm{Cu(AEP\text{-}Si}\equiv)]^{2+}$ and $[\mathrm{Cu(AEP\text{-}Si}\equiv)_2]^{2+}$ respectively).[8] Both complexes can be detected by UV-visible and ESR spectroscopies. Their characteristics are summarised in Table 2. Elemental analysis was performed after complexation and N/Cu molar ratios are reported in Table 1. Whatever the amount of grafted AEPTS from 1 to 22 wt%, the N/Cu molar ratio ranges between 2 and 4: this strongly indicates the presence of both complexes at the surface. To get direct evidence for that, UV-visible and ESR spectra were recorded on the various samples.

These two copper(II) complexes immobilised on silica gel can be identified by UV-visible spectroscopy because of the difference in their maximum absorption wavelength.[26] The deconvolution of the spectra (Fig. 3) provides the relative amount of each complex in the sample (Table 1). Both, 1 : 1 and 2 : 1 complexes are present at the surface for AEPTS/SiO$_2$ > 2 wt%, which is the limit of sensitivity of the UV-visible spectroscopy under our experimental conditions. The amount of $[\mathrm{Cu(AEP\text{-}Si}\equiv)_2]^{2+}$, which is dominant (80%) at high AEPTS coverage, progressively decreases with the AEPTS content to the benefit of $[\mathrm{Cu(AEP\text{-}Si}\equiv)]^{2+}$ (sample G: AEPTS/SiO$_2$ = 2wt%, $[\mathrm{Cu(AEP\text{-}Si}\equiv)_2]^{2+}$ = 25% and $[\mathrm{Cu(AEP\text{-}Si}\equiv)]^{2+}$ = 75%, Table 1). This means that Cu^{2+} occupies both sites depending on accessibility. Moreover, the decrease of the N/Cu molar ratio is in agreement with the relative decrease of the 2 : 1 complex observed from UV-visible spectroscopy.

Table 2 UV-visible and ESR parameters of $[\mathrm{Cu(AEP\text{-}Si}\equiv)]^{2+}$ and $[\mathrm{Cu(AEP\text{-}Si)_2}]^{2+}$ complexes from ref. 27 and 28

		$[\mathrm{Cu(AEP\text{-}Si)_2}]^{2+}$	$[\mathrm{Cu(AEP\text{-}Si)}]^{2+}$
Parameters	Color	Purple	Blue
Optical	λ/nm	550	660
ESR	A_z/cm^{-1}	16.9×10^{-3}	19.4×10^{-3}
	g_z	2.27	2.19

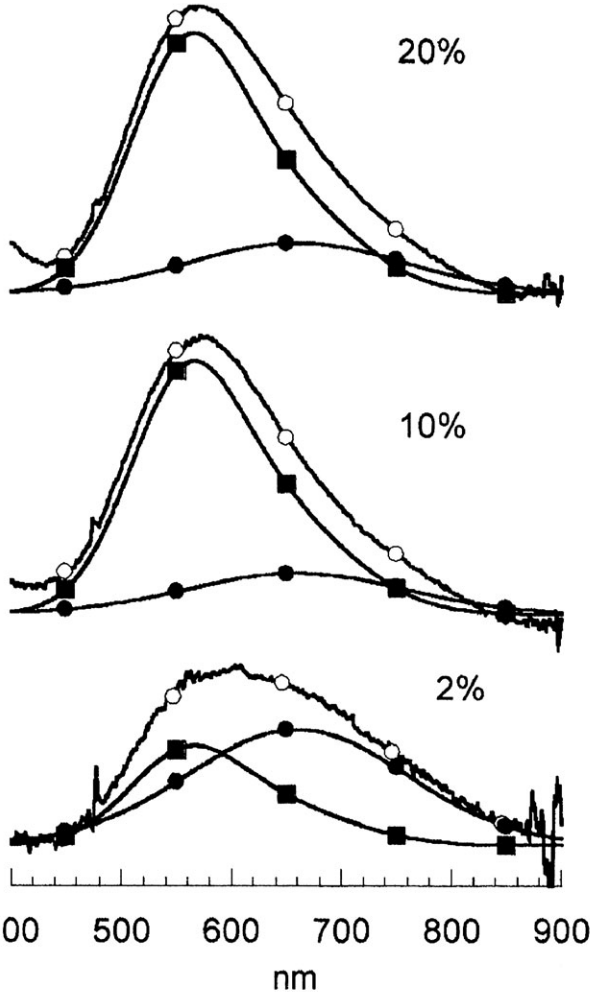

Fig. 3 UV-visible absorption spectra of a) sample B (AEPTS/SiO$_2$ = 20 wt%), b) sample C (AEPTS/SiO$_2$ = 10 wt%) and c) sample G (AEPTS/SiO$_2$ = 2 wt%). ○ experimental data, ■ $[\mathrm{Cu(AEP\text{-}Si)_2}]^{2+}$, ● $[\mathrm{Cu(AEP\text{-}Si)}]^{2+}$.

Below 2 wt% of alkoxysilanes on silica and for loadings down to 0.35 wt% of alkoxysilanes, ESR measurements could be performed. Typical spectra are shown in Fig. 4. For a 5 wt% alkoxysilanes concentration (Fig. 4a), the signal (g_z = 2.27 and A_z = 18.10^{-3} cm^{-1}) is assigned to the 2 : 1 complex in agreement with published values.[27,28] At lower coverage

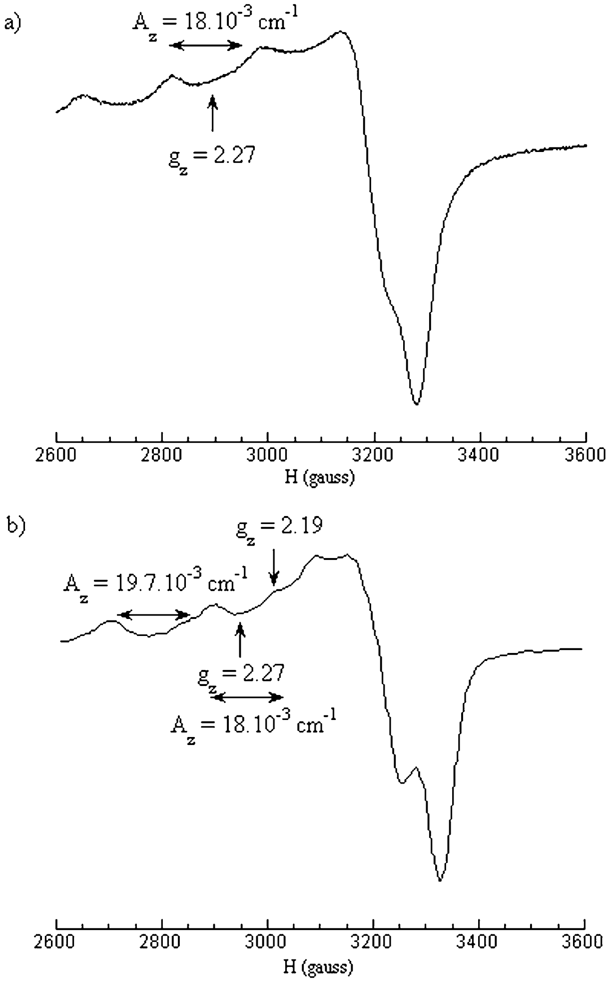

Fig. 4 ESR spectra of amine complexes of copper(II) immobilised on silica. a) Sample E (AEPTS/SiO$_2$ = 5 wt%) and b) sample H (AEPTS/SiO$_2$ = 1 wt%).

(Fig. 4b), a new signal appears (g_z = 2.19 and A_z = 19.7 × 10^{-3} cm^{-1}) which is likely related to the 1 : 1 complex. The ESR parameters do not correspond to those obtained for Cu(II) ions on silica surfaces that are assigned to the formation of Cu(OH)$_2$ species.[29] The observed species are clearly due to the formation of Cu(II) complexes with amino ligands. UV-visible spectroscopy provides quantitative information on the distribution of 1 : 1 and 2 : 1 Cu(II) complexes *versus* the surface coverage, whereas only qualitative information is given by ESR. Both spectroscopies indicate that, at low coverage, the 1 : 1 complex is predominant (Fig. 6A) and the amount of the 2 : 1 complex increases homogeneously with the surface coverage. The parameter $R = g_z/A_z$ could provide information regarding the geometry of the 2 : 1 complex. Gouteron *et al.*[30] have studied the variation of R as a function of ω, a characteristic distortion angle of the complex. It varies from 0° in square-planar geometry to 90° in tetrahedral geometry (Fig. 5). In our systems, the R value (126) corresponds to ω around 35°, which suggests a distorted square symmetry for the 2 : 1 complexes on the silica surface.

The concentration per surface unit of bonded alkoxysilanes could be calculated from both the elemental analyses and the specific surface area using the method proposed by Unger.[31,32]

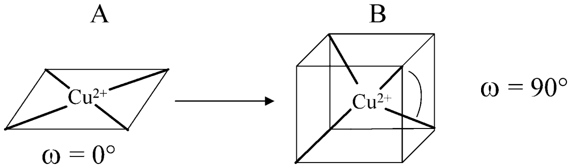

Fig. 5 Conformations of Cu^{2+} in (A) square-planar geometry or (B) tetrahedral geometry.

$$C\ (\mu\text{mol m}^{-2}) = W/(M \times S_{\text{BET}})$$

where W is the weight of the functional group (grams per gram of support), M is the molecular weight of the bonded aminosilane group (g mol^{-1}) and S_{BET} is the specific surface area of the support corrected by the weight increase due to the derivatization (m^2 g^{-1}). This equation assumes that the bonded groups are homogeneously distributed on the surface and the mean pore diameter of the support is about one order of magnitude larger than the molecular diameter of the alkoxysilanes. The average distance r between a bound alkoxysilane molecule and its nearest neighbour was calculated from the surface concentration.

$$r\ (\text{Å molecule}^{-1}) = (1/[C]N)^{1/2}$$

where $[C]$ is the surface concentration (mol m^{-2}) and N = 6.022 × 10^3 (molecules m^2 mol^{-1} Å^{-2}).[32,33] Results are given in Table 1. It appears that the average distance r between two alkoxysilanes decreases whereas the surface concentration C increases. Consequently, the loading of the surface provides a modification of the 2 : 1 complex geometry. Indeed, there are two possible conformations for this complex on the silica surface: the square-planar conformation (Fig. 6B), where the average distance between two alkoxysilanes is 5 Å and the area occupied by this alkoxysilane is analogous to that of an alkyltriethoxysilane (20 Å^2),[32,34] or the distorted square conformation (Fig. 6C). Because of the affinity of the amine function for the silica surface, the grafted molecule should fold up on itself on the surface. Then, to form the 2 : 1 complex, the average distance between two alkoxysilanes could vary from 5 to 10 Å. At low coverage, this distorted square conformation is most likely to occur (Fig. 6C), whereas the probability for the square-planar conformation (Fig. 6B) will increase with the surface loading. At very low coverage of the surface ($\leq$2 wt%), both signals are detected by ESR, which indicates that the $[\text{Cu(AEP-Si}{\equiv})_2]^{2+}$ complex is also present on the surface. The average distance between two alkoxysilanes calculated assuming a statistical distribution, is over 16 Å, which should not permit 2 : 1 complex formation. Two hypotheses can thus be proposed:

(1) The alkoxysilanes can be non-statistically distributed leading to the formation of islands on the silica surface, as suggested by Lochmüller *et al.*[33,35] It can result from a non-statistical distribution of the silanol groups, but also from specific chain–chain interactions that the alkoxysilane chains can develop during the grafting procedure, and which will influence their final relative position at the surface.

(2) The silanols can be statistically distributed as suggested by Unger *et al.*[31] However, the silica surface can present a

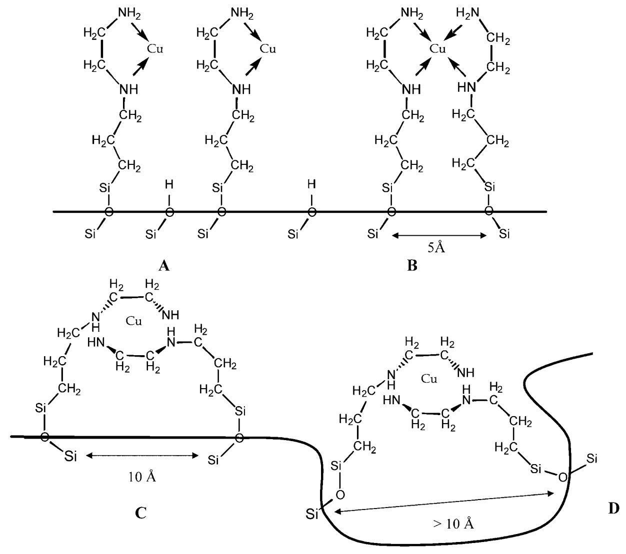

Fig. 6 Conformations of grafted silane: $[Cu(AEP\text{-}Si{\equiv})]^{2+}$ complex (A), $[Cu(AEP\text{-}Si{\equiv})_2]^{2+}$ complex in square-planar geometry (B) or distorded square-planar geometry (C and D).

fractal behaviour (as described by Avnir *et al.*[36]) with the presence of cavities (as illustrated in Fig. 6D). In that case, the 2 : 1 complex can be formed from two alkoxysilanes facing each other.

Conclusion

In this study, we have investigated the reaction between (3-aminoethyl)amino-propyltrimethoxysilane (AEPTS) and a precipitated silica in organic solvent. The main objective was to better characterise the distribution of grafted units at the surface of the silica particles, depending on the alkoxysilane coverage. This is why AEPTS was chosen, for its ability to form stable 1 : 1 and 2 : 1 complexes with Cu^{2+} ions ($[Cu(AEP\text{-}Si{\equiv})]^{2+}$ and $[Cu(AEP\text{-}Si{\equiv})_2]^{2+}$, respectively), that could trace back the proximity between the alkoxysilane entities. Original results have been obtained in terms of characterisation techniques. First, Karl Fischer titration has been used to quantify the surface silanols on the silica particles (3.5 OH nm^{-2}), and thus to estimate the amount of alkoxysilane that leads to the formation of one monolayer (20 wt% of AEPTS with respect to SiO_2). Then a ^{29}Si solid-state MAS NMR study combining CP and SPE experiments led to the quantification of the grafted units, even when a too low concentration prevented the detection of these units in the SPE spectrum. The results were then compared with elemental analysis and revealed excellent agreement. Finally, complexation with Cu^{2+} ions was studied to evaluate the spatial distribution of the grafted units at the surface. UV-visible and ESR spectra revealed the existence of both complexes ($[Cu(AEP\text{-}Si{\equiv})]^{2+}$ and $[Cu(AEP\text{-}Si{\equiv})_2]^{2+}$) in a large range of concentrations from 0.5 to 50% (w/w); the presence of the 2 : 1 complex at low concentration strongly suggests a non-statistical distribution of silanols at the surface and/or the presence of surface cavities in which silanols can be spatially close enough to allow complex formation. In both cases, the resulting picture of the functionalized surface is more one of high-density patches of grafted units than the uniform and relatively ordered alkoxysilane coverage that is commonly envisioned.

Acknowledgements

The authors acknowledge the financial support of Rhodia Recherches (Aubervilliers, France). B. Morin (LRS, UPMC, Paris, France) is also acknowledged for his technical assistance with the ESR experiments.

References

1 D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Laspéras, P. Moreau, F. D. Renzo, A. Galarneau and F. Fajula, *Coord. Chem. Rev.*, 1998, **178–180**, 1085.
2 J. F. Biernat, P. Konieczka, B. J. Tarbet, J. S. Bradshaw and R. M. Izatt, *Sep. Purif. Methods*, 1994, **23**, 77.
3 A. C. Franville, D. Zambon and R. Mahiou, *Chem. Mater.*, 2000, **12**, 428.
4 T. Czuryszkiewicz, J. Ahvenlammi, P. Kortesuo, M. Ahola, F. Kleitz, M. Jokinen, M. Linden and J. B. Rosenholm, *J. Non-Cryst. Solids*, 2002, **306**, 1.
5 P. Eaton, P. Holmes and J. Yarwood, *Appl. Spectrosc.*, 2000, **54**, 508.
6 D. L. Eaton, *Midl. Macromol. Monogr.*, 1980, **7**, 201.
7 M. Etienne and A. Walcarius, *Talanta*, 2003, **59**, 1173.
8 H. B. Jonassen and T. H. Dexter, *J. Am. Chem. Soc.*, 1949, 1553.
9 R. J. P. Corriu, C. Hoarau, A. Mehdi and C. Reyé, *Chem. Commun.*, 2000, 71.
10 R. J. P. Corriu, F. Embert, Y. Guari, A. Mehdi and C. Reyé, *Chem. Commun.*, 2001, 1116.
11 R. C. Smith and G. E. Kellum, *Anal. Chem.*, 1966, **38**, 67.
12 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.*, 2002, **40**, 70.
13 E. F. Vansant, P. Van der Voort and K. C. Vrancken, *Characterisation and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam, 1995, p. 79.
14 D. W. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.*, 1983, **105**, 1487.
15 M. L. Hair and C. P. Tripp, *NATO ASI Ser., Ser. 3*, 1996, **12**, 209.
16 I.-S. Chuang and G. E. Maciel, *J. Am. Chem. Soc.*, 1996, **118**, 401.
17 S. Léonardelli, L. Facchini, C. Fretigny, P. Tougne and A. P. Legrand, *J. Am. Chem. Soc.*, 1992, **114**, 6412.
18 J. B. Peri and A. L. Hensley, Jr, *J. Phys. Chem.*, 1968, **72**, 2926.
19 L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, 1997, **9**, 500.
20 R. Mueller, H. K. Kammler, K. Wegner and S. E. Pratsinis, *Langmuir*, 2003, **19**, 160.
21 L. T. Zhuravlev, *Colloids Surf., A*, 2000, **173**, 1.
22 B. A. Morrow and A. J. Mc Farlan, *Langmuir*, 1991, **7**, 1695.
23 K. Fischer, *Angew. Chem.*, 1935, **26**, 394.
24 H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, 1951, **73**, 2367.
25 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 1973, **59**, 569.
26 R. S. Field, D. E. Leyden and R. S. S. Murthy, *Anal. Chim. Acta*, 1986, **186**, 123.
27 V. B. Golubev, G. V. Kudryavtsev, G. V. Lisichkin and D. V. Mil'chenko, *Russ. J. Phys. Chem. (Transl. of Zh. Fiz. Khim.)*, 1985, **59**, 1674.
28 T. J. Pinnavaia, J. G. S. Lee and M. Abedini, *Midl. Macromol. Monogr.*, 1980, **7**, 333.
29 K. Xia, A. Mehadi, R. W. Taylor and W. F. Bleam, *J. Colloid Interface Sci.*, 1997, **185**, 252.
30 J. Gouteron, S. Jeannin, Y. Jeannin, J. Livage and C. Sanchez, *Inorg. Chem.*, 1984, **23**, 3387.
31 K. K. Unger and P. Roumeliotis, *J. Chromatogr.*, 1978, **149**, 211.
32 S. R. Wasserman, G. M. Whitesides, I. Tidswell, B. M. Ocko, P. S. Pershan and J. D. Axe, *J. Am. Chem. Soc.*, 1989, **111**, 5852.
33 C. H. Lochmüller, A. S. Colborn, M. L. Hunnicutt and J. M. Harris, *Anal. Chem.*, 1983, **55**, 1344.
34 A. Ulman, *Adv. Mater.*, 1990, **2**, 573.
35 C. H. Lochmüller, A. S. Colborn, M. L. Hunnicutt and J. M. Harris, *J. Am. Chem. Soc.*, 1984, **106**, 4077.
36 D. Avnir, D. Farin and P. Pfeifer, *Nature*, 1984, **308**, 261.