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New bonding modes of gas-phase deposited γ-aminopropyltriethoxysilane on silica studied by ^{29}Si CP/MAS NMR

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Besides the well-known reaction between the ethoxy groups of the silane end of the γ-aminopropyltriethoxysilane (APTS) molecule and the silanols of silica, the amino ends of APTS molecules were observed to react in the gas phase with ethoxy groups of other APTS molecules and silanols of silica at elevated temperatures on the silica surface, dehydroxylated at 600 °C, forming Si–N linkages, as established by ^{29}Si CP/MAS NMR.

Amino-functionalized overlayers on silicon dioxide surfaces are widely used in analytical chemistry, biochemistry, catalyst technology and electronics.[1] One of the main applications for aminosilylated porous silica is its use as a stationary phase in chromatography.[1,2] The preparation of amino-terminated surfaces is mostly performed through liquid-phase reactions with aminoalkoxysilanes as precursors, organic solvent techniques being industrially the most important and therefore frequently studied.[1] In contrast, very few studies on the gas-phase deposition of aminosilanes on silica have been published.[3–5]

Nevertheless, the gas-phase deposition of aminosilane overlayers on silica offers major advantages. Exploiting gas-phase techniques eliminates many of the tedious operations of the liquid-phase methods, such as controlled hydrolysis of alkoxy groups, solvent removal and recovery, and washing procedures.[6] The presence of water has a significant influence on the mechanism of overlayer formation and further on the structure of the surface species formed. In the gas phase water molecules can be easily excluded from the deposition process. In our study, the deposition of APTS on a dehydroxylated silica surface† was performed by a surface-limiting gas-phase technique, atomic layer deposition, ALD.[7] By ALD molecular layers can be reproducibly deposited onto a solid support in a very controlled and conformal manner.[8]

The principal reaction of vaporized APTS molecules with the silanol groups of silica has been earlier observed to occur through the ethoxy groups of the silane end of the molecule resulting in a formation of siloxane groups at a reaction temperature of 150 °C (20–50 mbar).[3,5] According to the present ^{29}Si CP/MAS NMR‡ study trifunctional APTS is observed to be bound onto silica surface, pretreated at 600 °C, both through one ($\delta = -53$ ppm) and two ethoxy groups forming siloxane bridges ($\delta = -59$ ppm) (Fig. 1), as has been earlier observed for silica pretreated at 450 °C.[3] Mono- and bidentate bonding modes of APTS on silica are shown in Fig. 2a and 2d. The chemical shifts of these peaks have been generally accepted in the solid-state NMR studies performed for samples deposited in the liquid[9,10] or gas phase.[3] The relative number of monodentate species of APTS molecules on silica compared to the number of bidentate species is observed to increase when the deposition temperature is raised from 150 to 200 °C. However, this trend cannot be observed when the reaction temperature is further raised to 300 °C. A shoulder at −50 ppm (Fig. 2c) next to the peak at −53 ppm in the spectrum for APTS deposited at 300 °C on silica is likely due to minor hydroxylation of free ethoxy groups for monodentate-wise bound APTS molecules.

When the deposition temperature of APTS on silica is increased from 150 °C to 300 °C, new peaks appear or small peaks increase in intensity in the ^{29}Si CP/MAS NMR spectra (Fig. 1). At the reaction temperature of 150 °C a completely new resonance at −40 ppm (Fig. 2e) is observed which has not been observed earlier in the APTS samples deposited onto silica in the liquid phase.[9,10] This peak can be assigned to silicon atoms surrounded by three oxygen atoms of the ethoxy groups. The resonance of neat APTS in deuterochloroform in the solution-state ^{29}Si NMR spectrum is seen at −45.4 ppm.[9,11] Free APTS molecules are unlikely to be physisorbed onto the pores of silica because of the use of elevated reaction temperatures and nitrogen purging of possibly physisorbed molecules in the ALD reactor. Thus, APTS molecules are likely to be bound through the amino end. In addition, at the deposition temperatures of 200 and 300 °C a group of new bands appear at −33, −27 and −20 ppm (Fig. 1). These bands and the band at −40 ppm can be assigned to $–CSi(OEt)_n(NH)_{3-n}–$ species (n = 0,1,2 or 3) on silica (Fig. 2e, f, h, i) which are due to the reaction of ethoxy groups and amino groups of APTS molecules on silica.

Caravajal *et al.*[9] have suggested several possible surface species for APTS molecules on silica when the deposition is performed in the liquid phase. According to our FTIR study hydrogen-bonding interactions between amino and silanol groups are also observed in the aminosilylated silica samples deposited in the gas phase.[5] According to Caravajal *et al.*[9] and Vansant *et al.*[1] the amino group of aminosilanes can possess

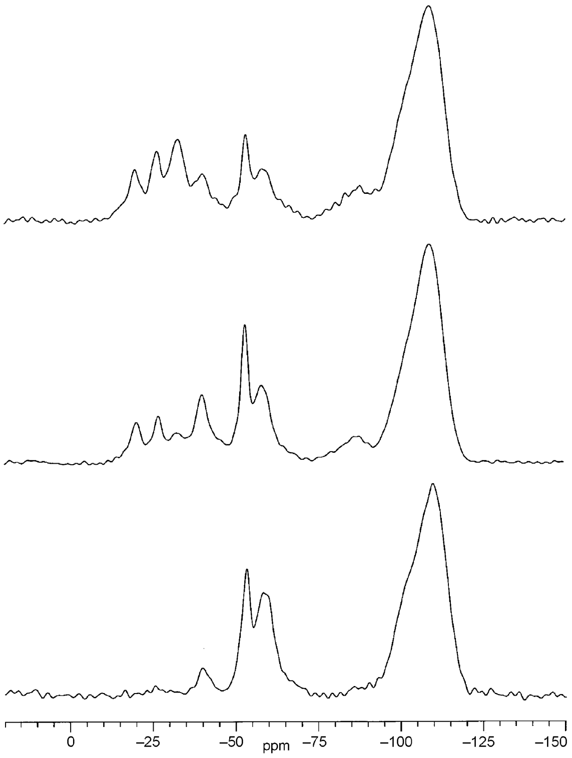

Fig. 1 ^{29}Si CP/MAS NMR spectra (from bottom to top) of silica treated with vaporized APTS at 150, 200 and 300 °C.

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ionic interactions with the silanols of silica forming proton-transfer complexes. Nevertheless, covalent bonds between nitrogen and silicon atoms have not been observed with aminopropylalkoxysilanes deposited in organic solvents on silica. According to the present study the use of high reaction temperatures, *i.e.* 150–300 °C, in the gas-phase deposition of APTS on silica enables the formation of Si–N bonds. In addition to the frequencies of the amino group ($-NH_2$) at 3380 and 3305 cm^{-1}, new bands at 3470 and 3435 cm^{-1} due to the ≡Si–NH–C– moiety appear.[5] The surface density of nitrogen atoms, *i.e.* adsorbed APTS molecules,§ on silica decreases from 1.6 molecules nm^{-2} to 0.8 molecules nm^{-2} (51%) when the deposition temperature is increased from 150 °C to 300 °C. Thus, the number of surface species on silica decreases when the deposition temperature is increased. At the same time, a decrease in the number of carbon atoms from 7.6 atoms nm^{-2} to 3.3 atoms nm^{-2} (57%) is observed. The carbon/nitrogen ratio also decreases from 4.9 to 4.3 when the deposition temperature is increased which also indicates that a larger number of ethoxy groups react or decompose on the surface at higher reaction temperatures. Decomposition of triethoxysilane, $HSi(OEt)_3$, has been observed to begin at temperatures near 300 °C judging from the decrease in the carbon content in the samples and appearance of the O–H stretching band at about 3750 cm^{-1} in the DRIFT spectrum.[12] The appearance of this band for free silanols in the DRIFT spectrum was also observed for APTS deposited at 300 °C on silica indicating decomposition of ethoxy groups and other surface structures on silica.

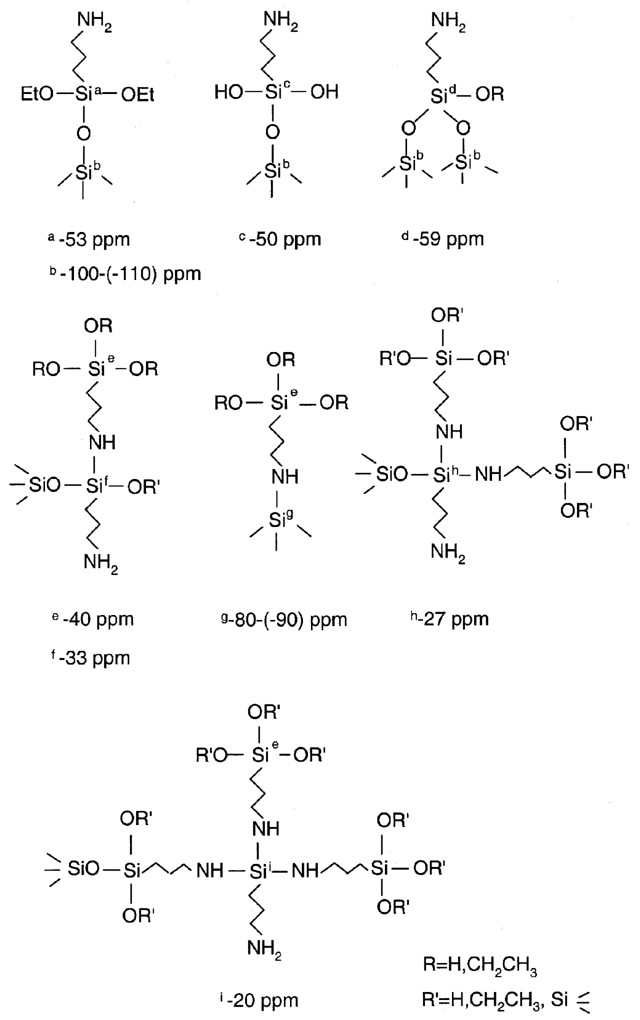

Fig. 2 Surface species of APTS vapour on silica (Si≡ represents the silica surface).

It was shown above that the amino groups of APTS molecules react with the alkoxy groups of other APTS molecules on silica at high deposition temperatures. In addition, an indication of the reaction between the amino groups of APTS molecules with silanol groups of silica or strained siloxane bridges[13] was observed. The presence of O_3–Si–N surface species can be observed at −80–(−90) ppm (Fig. 1 and Fig. 2g) already at the deposition temperature of 150 °C and even more so at higher deposition temperatures, *i.e.* at 200 and 300 °C, when part of the SiO_4 species at −100–(−110) ppm (Fig. 1 and 2b) have shifted to higher frequency due to the substitution of one oxygen for a nitrogen.[14] The present study shows that deposition temperatures ≤150 °C should be used to avoid the secondary reactions of amino groups on the silica surface.

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Notes and references

† APTS (> 97–99%), $NH_2(CH_2)_3Si(OEt)_3$, was used as received from Merck, Germany. The average surface area of silica, EP10$_x$ from Crosfield Ltd., UK, was 300 $m^2\ g^{-1}$, pore volume 1.2 $cm^3\ g^{-1}$ and pore diameter 20 nm, and particle size 100 µm.

‡ The ^{29}Si CP/MAS NMR spectra (Fig. 1) were acquired on a Chemagnetics CMX Infinity 270 MHz NMR spectrometer using a 5 ms contact time, 5 s recycle delay, rf fields of about 30 kHz and spinning speeds around 3.5 to 4.0 kHz. Chemical shifts (δ) were observed at −40 ppm (Fig. 2e), −53 ppm (Fig. 2a), −59 ppm (Fig. 2d), −80–(−90) ppm (O_3SiN, Fig. 2g) and −100 to −110 ppm (O_4–Si, Fig. 2b) for all samples deposited at 150–300 °C, and at 200–300 °C additionally at −33, −27 and −20 ppm (Fig. 2f, h and i). There is also a shoulder at −50 ppm in the spectrum of APTS deposited at 300 °C (Fig. 2c).

§ Elemental analyses were performed in the LECO CHN-600 analyser. The results were 1.56, 1.33 and 0.76 N atoms nm^{-2} and 7.62, 6.37 and 3.25 C atoms nm^{-2} for samples deposited at 150, 200 and 300 °C, respectively.

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