A ^{29}Si and ^{13}C CP/MAS NMR Study on the Surface Species of Gas-Phase-Deposited γ-Aminopropylalkoxysilanes on Heat-Treated Silica

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The aim of the present solid-state NMR study was to characterize the surface species of γ-aminopropyltriethoxysilane (APTS), γ-aminopropyltrimethoxysilane (APTMS), and γ-aminopropyldiethoxymethylsilane (APDMS) on porous silica when the deposition was performed via the gas phase. The reaction temperature used, that is, 150−300 °C, in an atomic layer deposition reactor at a pressure of 20−50 mbar, was observed to distinctly affect the surface species of aminopropylalkoxysilanes on silica. The gas−solid reactions of the precursors with the silica surface were observed to be surface-limiting at the deposition temperatures of ≤150 °C. On the basis of ^{29}Si CP/MAS NMR, the amino ends of APTS and APTMS molecules were observed to react both with alkoxy groups of other precursor molecules and silanols of silica at deposition temperatures of ≥150 °C forming Si−N linkages. The amino groups of APDMS molecules were observed to react at 150 °C only on silica heat-treated at 200 °C in a similar way. The reaction of amino groups affected also the chemical shifts of the carbon atoms in the propyl chain causing splitting of the peaks in the ^{13}C CP/MAS NMR spectra. At still higher reaction temperatures, especially at 300 °C, decomposition of the surface structures was observed to occur. The bonding modes of trifunctional APTS and bifunctional APDMS on silica heat-treated at 200−800 °C were systematically studied by ^{29}Si and ^{13}C NMR when the deposition was performed at 150 °C. Bi- and tridentate species of APTS were observed on silica pretreated at 200 °C, and mono- and bidentately bound surface structures were observed when silica was heat-treated at 450−800 °C. APTMS was also observed to attach onto silica pretreated at 600 °C in a similar way. APDMS was bound both mono- and bidentately on silica pretreated at 200 °C and at 600−800 °C but solely bidentately on silica pretreated at 450 °C.

1. Introduction

Aminosilylated silicon dioxide surfaces have widespread applications, for example, in analytical chemistry as stationary phases and as metal ion sorbents, in biochemistry for the immobilization of enzymes, in heterogeneous catalysis, and in electronics as chemical sensors and semiconductor devices.[1] Silylation of surfaces is usually performed via the liquid phase on both industrial and laboratory scale. The gas-phase deposition of γ-aminopropylalkoxysilanes on silica has recently been studied by using elemental analyses, diffuse reflectance Fourier infrared spectroscopy (DRIFTS), and to some extent also ^{13}C NMR employing cross-polarization (CP) and magic-angle spinning (MAS) as characterization techniques.[2−7] However, no systematic characterization of the surface species of the gas-phase-deposited γ-aminopropylalkoxysilanes on silica has been performed. Useful but limited information on the bonded species of silylated silica surfaces can be obtained through the above-mentioned techniques and also thermoanalytical methods.[8] Only the use of ^{29}Si CP/MAS NMR and additionally ^{13}C CP/MAS
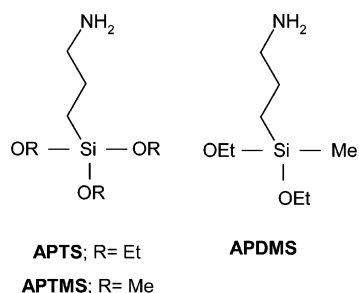
NMR enables a thorough characterization of the surface species on silylated silica, however. Several solid-state NMR studies have been performed on silica gel[8−19] and fumed silica[9,18] modified with alkoxysilanes through the liquid phase for the successful detection of the surface species. Especially, a useful solid-state NMR study on the reactions and surface species of APTS and 3-metacryloxypropyltrimethoxysilane (MPS) deposited in various solvents onto porous silica has been performed by De Haan et al.[9] The aim of the present study was to thoroughly characterize the surface species on silica with different degrees of dehydroxylation when it was modified with bi- and trifunctional aminopropylalkoxysilanes from the gas phase at various deposition temperatures. Atomic layer deposition (ALD) technique[20−24] was applied for the deposition of one surface-saturated molecular layer of precursor molecules onto the silica surface.

2. Experimental Section

2.1. Chemical Reagents. For the preparation of aminosilylated surfaces, γ-aminopropyltriethoxysilane (APTS) from Merck, Germany, γ-aminopropyltrimethoxysilane (APTMS)

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CHART 1

APTS; R= Et

APTMS; R= Me

APDMS

TABLE 1: Reaction Conditions in the Gas-Phase Deposition of Aminopropylalkoxysilanes on Silica

precursor	vaporization temperature/°C	reaction temperatures/°C			
APTS	120–130		150	200	300
APTMS	90–110		150	250	
APDMS	110–120	125	150	200	300

from Aldrich, United States, and ABCR, Germany, and γ-aminopropyldiethoxymethylsilane (APDMS) from ABCR, Germany, were used as precursors (Chart 1). Purity of the reagents, as reported by the manufacturers, was >97–99%, and it was also checked through liquid-phase NMR measurements. The reagents were used as received.

2.2. Silica Surfaces. EP 10$_x$ silica gel from Crosfield Ltd, United Kingdom, was used as a support. It had a BET (Brunauer–Emmett–Teller) surface area of 300 m^2/g, a pore volume of 1.2 cm^3/g, and a pore diameter of 20 nm. The average particle size of silica was 100 μm. When silica was pretreated at 800 °C, the BET surface area was diminished to 280 m^2/g and pore volume to 1.0 cm^3/g. For the BET measurements, silica gel was degassed at 350 °C in a vacuum (10^{-6} Torr), and the determinations were performed using nitrogen as the adsorbate. Silica was pretreated at 200, 450, 600, and 800 °C for 16 h in a muffle furnace in air prior to the deposition of precursors on the surface.

2.3. Gas-Phase Depositions. Precursors were deposited onto porous silica via the gas phase by atomic layer deposition technique.[20–24] First, heat-treated silica (4–5 g) was pretreated in an ALD reactor (F-120, ASM Microchemistry Ltd., Espoo, Finland) at 150–180 °C for the removal of physisorbed water from the surface. The precursors were vaporized at 90–130 °C at a pressure of 20–50 mbar. At a reaction temperature of 150 °C, the gas–solid reactions were surface-limiting resulting in characteristic ALD-type growth. Precursors were deposited at 150 °C onto silica pretreated at 200, 400, 600, and 800 °C. The deposition process was also studied at various reaction temperatures on silica pretreated at 600 °C (Table 1). The deposition of APTS and APDMS onto silica was also studied at the reaction temperatures of 200 and 300 °C and APTMS at 250 °C. In addition, the deposition of APDMS on silica was studied at a lower temperature, that is, 125 °C. Physisorbed precursor molecules were purged from the surface with inert nitrogen gas after which only chemisorbed precursor molecules remained on the surface. Aminosilylated silica samples were stored in a desiccator to avoid hydrolysis of the alkoxy groups because of air humidity.

2.4. Carbon and Nitrogen Analyses. The numbers of carbon and nitrogen atoms in the modified silica samples were calculated from the results of elemental analyses carried out in a LECO CHN-600 elemental analyzer.

2.5. ^{29}Si and ^{13}C CP/MAS NMR Measurements. *2.5.1. Equipment A.* Solid-state ^{13}C and ^{29}Si CP/MAS NMR spectra were recorded on a Chemagnetics CMX270 Infinity spectrom-

eter. The powder samples were inertly handled under dry nitrogen and placed in zirconia rotors of 10 mm o.d. The ^{13}C CP/MAS spectra were obtained at a spinning speed around 4.0 kHz using rf fields of 32 kHz (8 μs 90° pulses), a contact time of 2 ms, and a recycle delay of 5 s. Between 2000–12 000 transients were acquired. The chemical shifts are reported relative to TMS using an external sample of hexamethylbenzene (methyl groups at +17.35 ppm). ^{29}Si NMR CP/MAS spectra were measured at a spinning speed of around 4.0 kHz using rf fields of 32 kHz (8 μs 90° pulses), a contact time of 5 ms, and a recycle delay of 5 s. Between 15 000–49 000 transients were acquired. The chemical shifts are reported relative to TMS using an external sample of sodium trimethylsilyl propanesulfonate (Sigma-Aldrich) (at +1.6 ppm).
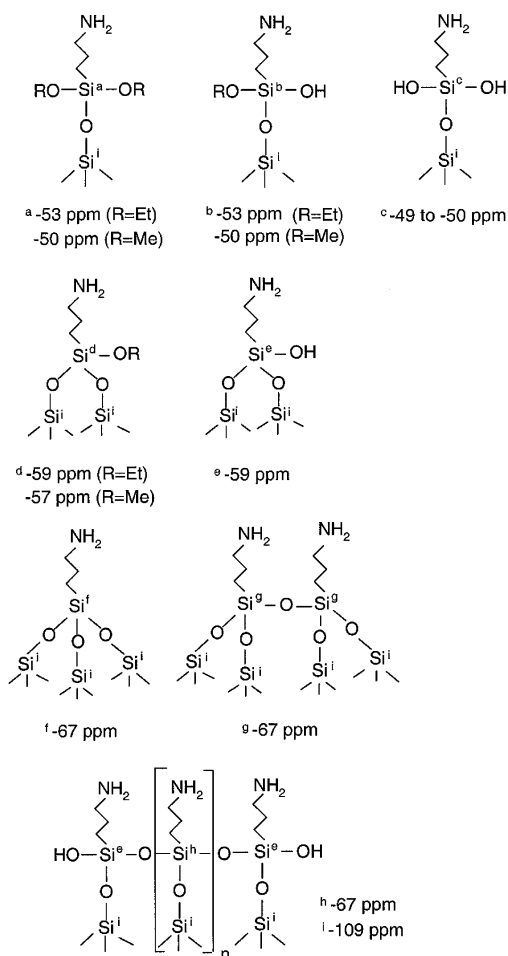
2.5.2. Equipment B. Solid-state ^{13}C and ^{29}Si CP/MAS NMR spectra were recorded on a Bruker AMX 400 standard bore, high-resolution NMR spectrometer operating at 100.6 and 79.49 MHz, respectively. The powder samples were placed in zirconia rotors of 7 mm o.d. The ^{13}C CP/MAS spectra were obtained at a spinning speed of 4.5 kHz using a 50 kHz spectral width (5.8 μs 90° pulses), a contact time of 3 ms, and a recycle delay of 4 s. Transients of 14 000 were acquired. The chemical shifts are reported relative to TMS using an external sample of glycine as reference (methylene group at 43.2 ppm). ^{29}Si NMR CP/MAS spectra were measured at a spinning speed of 4.5 kHz using a 30 kHz spectral width (5.6 μs 90° pulses), a contact time of 5 ms, and a delay of 5 s. The ^{29}Si NMR spectra were recorded with 16 000 transients. The chemical shifts are reported relative to TMS using an external reference of trimethylsilyl ester of cubic octameric silicate, [(CH$_3$)$_3$Si]Si$_8$O$_{20}$ (Academie der Wissenschaften der DDR) (Si–Me at +12.2 ppm).

3. Results and Discussion

The principal reaction of γ-aminopropylalkoxysilanes from the gas or liquid phase occurs through the silane end of the precursor molecule with the silanol groups of silica.[2] Then, the alkoxy groups react with the silanols forming siloxane bridges. On the basis of our previous study, isolated silanols seem to selectively react with vaporized aminopropylalkoxysilanes under saturation conditions, namely, at a reaction temperature of 150 °C and a pressure of 20–50 mbar.[2] The amino or alkoxy groups of chemisorbed precursor molecules interact with the surface Si–OH groups forming hydrogen bonds.[2] The amino groups have also been observed to possess ionic interactions with the silanols when the precursor has been deposited on silica from the liquid phase.[1,11]

The chemical nature of the surface species of gas-phase-deposited aminopropylalkoxysilanes on silica is especially dependent on the reaction conditions, that is, the deposition temperature, and surface species of the silica surface. Also, the presence of water has a great influence on the deposition process. However, water molecules can be excluded from the gas-phase process because of the use of reduced pressure and elevated temperatures. The surface species on silica can be altered through heat treatment.[1] At low pretreatment temperatures of silica (<450 °C), there are more H-bonded silanols than isolated silanols on the surface. When the pretreatment temperature of silica is increased to 800 °C, there are no hydrogen-bonded silanols on the silica surface. The exact numbers of isolated and hydrogen-bonded silanols on heat-treated silica can be found in the literature.[25] At high pretreatment temperatures of silica, that is, >450 °C, strained siloxane bridges also appear on the surface.[1] They are involved in the reaction with alkoxysilanes[14] and thus aminopropylalkoxysilanes are also likely to react with strained siloxanes on silica.

CHART 2

a -53 ppm (R=Et)
-50 ppm (R=Me)

b -53 ppm (R=Et)
-50 ppm (R=Me)

c -49 to -50 ppm

d -59 ppm (R=Et)
-57 ppm (R=Me)

e -59 ppm

f -67 ppm

g -67 ppm

h -67 ppm
i -109 ppm

Figure 1. ^{29}Si CP/MAS NMR spectra (measured with equipment A) of APTS deposited onto silica pretreated at 600 °C at reaction temperatures of (a) 150 °C (15 000 scans), (b) 200 °C (49 000 scans), and (c) 300 °C (48 000 scans).

In the present study, the surface species of gas-phase-deposited γ-aminopropylalkoxysilanes on silica were studied by solid-state NMR techniques. The ^{29}Si NMR gives useful information on the coordination at the silicon atoms of the silane molecules and in the silica gel.[1] On the other hand, the ^{13}C NMR gives additional information on the reactions of alkoxy groups, that is, presence or absence of free alkoxy groups, on the silylated silica surface. The ^{13}C NMR can also be used to study the chemical interactions of the amino group of aminopropylalkoxysilanes with other atoms because they cause electric field effects on the chemical shifts of carbon atoms, especially on the carbon atom in the middle of the propyl chain.[11] The solid-state NMR measurements performed are only of qualitative nature because no calibration between the intensities of NMR peaks and the concentrations of the surface species was made. In particular, the effects of gas-phase-deposition temperature of aminopropylalkoxysilanes and pretreatment temperature of silica on the surface species formed are discussed below.

3.1. Effect of Reaction Temperature on the Surface Species of Gas-Phase-Deposited γ-Aminopropylalkoxysilanes on Silica. *3.1.1. APTS Deposited at 150−300 °C on Silica Heat-Treated at 600 °C.* According to the previous[3,6] and present ^{29}Si CP/MAS NMR studies, trifunctional γ-aminopropyltriethoxysilane molecules are observed to be mainly bound from the silane end of the molecule with the silanols of silica, pretreated at 450−600 °C, both through one and two ethoxy groups forming siloxane bridges at saturation conditions (Chart 2a and d). Saturation of silica with vaporized APTS molecules has been achieved at relatively low deposition temperatures, that is, near 150 °C.[2,3] Mono- and bidentate bonding modes of
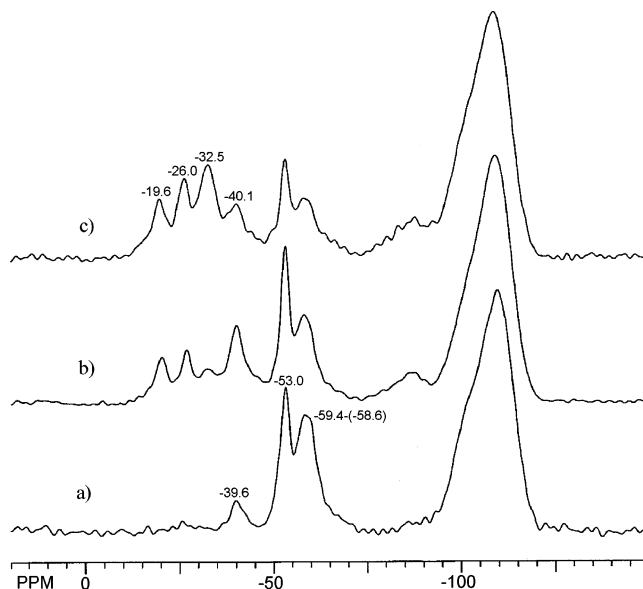
APTS on silica pretreated at 600 °C are seen in the ^{29}Si CP/MAS NMR spectrum (Figure 1) regardless of the deposition temperature, that is, 150−300 °C, as chemical shifts at $\delta = -53$ ppm and $\delta = -59$ ppm[1,6,10−13] (Table 2), respectively. Additionally, a small shoulder approximately at −50 ppm next to the peak at −53 ppm is observed in the spectrum where APTS has been deposited on silica at 300 °C (Figure 1c). This may be due to minor hydrolysis of free ethoxy groups, that is, formation of OH groups, for monodentately bound APTS molecules (Chart 2c) or, on the other hand, it may be due to the decomposition of ethoxy groups. Hydrolysis of APTS-treated silica is further discussed in section 3.2.

When the deposition temperature of APTS on silica pretreated at 600 °C 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 (Figure 1). At the reaction temperature of 150 °C, a completely new resonance at −40 ppm is observed which has not been observed earlier in the ^{29}Si NMR spectra of APTS samples deposited onto silica in the liquid phase.[1,9−11] We postulate that this peak is due to the silicon atom of the silane molecule surrounded by three unreacted ethoxy groups. For comparison, the resonance of liquid APTS in deuteriochloroform (CDCl$_3$) in the solution-state ^{29}Si NMR spectrum is seen at −45.4 ppm.[10,11] However, 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 after the surface reaction in the ALD reactor. Thus, APTS molecules are likely to be bound through the amino end of the molecule when all three alkoxy groups remain unreacted on the surface. In addition, at the deposition temperatures of 200 and 300 °C, a group of new bands appear at −33, −26, and −20 ppm (Figure 1, Table 3). Very faint peaks at the same positions are also seen at the deposition temperature of 150 °C. We postulate that these peaks can also be assigned to species (Chart 3c−e) formed in the reaction of amino groups with one, two, or three ethoxy groups of APTS molecules on silica.

In addition to the reaction with the alkoxy groups, the amino group was also observed to react with the silanol groups of silica (Chart 3a). The presence of O$_3$−Si−N surface species, seen

TABLE 2: ^{29}Si CP/MAS NMR Results on APTS and APDMS (and APTMS) Deposited at 150 °C on Heat-Treated Silica and Results from the Gas- and Liquid-Phase Literature Studies

|			chemical shifts/ppm				
precursor	ref	pretreatment of silica/°C	monodentate bonding	bidentate bonding	tridentate bonding	additional peak[a]	liquid-NMR results
APTS		200		−59.9	−68.0		
APTS		450	−52.8	−59.6 to −58.9		−39.7	
APTS		600	−53.0	−59.4 to −58.6		−39.6	
APTS		800	−53.0	−59.3 to −57.4		−39.7	
APTS	6	450	−52	−58			
APTS	9	190	−53 to −54	−58 to −59	−66 to −67		
APTS	11	25−200	−49	−58	−66		
APTS	10						−45.4
APDMS		200	−13.2	−15.9		−5.7	
APDMS		450		−19.1			
APDMS		600	−12 to −13	−17 to −19			
APDMS		800	−12.0	−19 to −20			
APDMS	1	not mentioned	−12.4	−19.7			
APDMS							−5.8
APTMS		600	−50.0	−56.5		−38.2	
APTMS	29, 30						−42.2, −41.8

[a] This peak is due to silicon atoms linked to three alkoxy groups.

TABLE 3: The Additional Peaks in the ^{29}Si CP/MAS NMR Spectra of APTS, APTMS, and APDMS Deposited at 150−300 °C on Heat-Treated Silica

precursor	pretreatment of silica/°C	chemical shifts/ppm					
APTS	600	−19.6	−26.0	−32.5	−40.1	−80.0, −83.5, −87.1	
APTMS	600	−19.8	−25.0	−32.9	−38.5	−79.9, −87.1	
APDMS	600	(+7.4)	+2.5	−5.0		−86.3 to 88.1	

approximately from −80 to −90 ppm (Figure 1, Table 3), confirms that the silanols react with the amino groups. O_3−Si−N species are seen already at the deposition temperature of 150 °C and even more so at higher deposition temperatures, that is, at 200 and 300 °C. Then, part of the SiO_4 species at about −100 to −110 ppm have shifted to higher frequency because of the substitution of one oxygen for a nitrogen.[26] The silanediol, silanol, and siloxane groups on silica are generally seen as a broad peak in the ^{29}Si NMR spectra at −90.6, −99.8, and −109.3 ppm, respectively.[27] The last two of these peaks can clearly be observed in our spectra.

The surface density of nitrogen atoms on silica, after treatment with APTS, decreases from 1.6 molecules/nm^2 to 0.8−1.2 molecules/nm^2 (25−51%) when the deposition temperature is increased from 150 °C to 300 °C (Table 4). Thus, the number of surface species of APTS decreases on silica when the deposition temperature is increased. At the same time, a diminishment in the number of carbon atoms from 7.6 atoms/nm^2 to 3.3−5.3 atoms/nm^2 (30−57%) was observed. The carbon/nitrogen ratio also decreases from 4.8 to 4.1−4.4 when the deposition temperature is increased which also indicates that

CHART 3
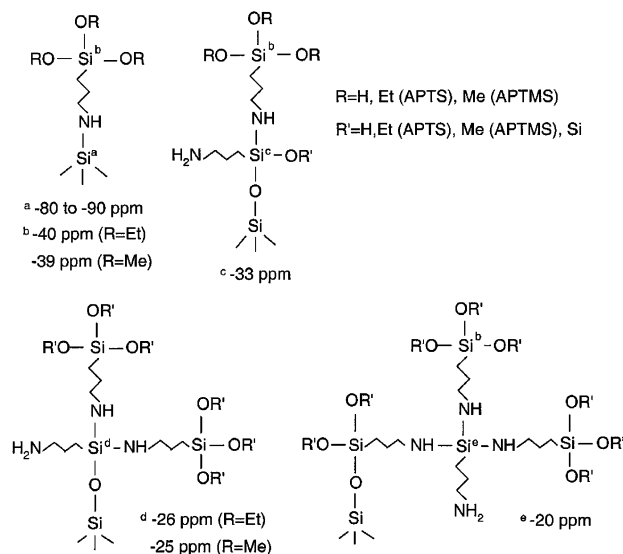
a larger number of ethoxy groups react or decompose on the surface at higher reaction temperatures. Decomposition of triethoxysilane, HSi(OEt)$_3$, has been observed to begin at temperatures near 300 °C judging from the decrease of the carbon content in the samples and appearance of the O−H stretching band at about 3750 cm^{-1} in the DRIFT spectrum.[28] The appearance of this OH band for isolated silanols in the DRIFT spectrum was also observed for APTS deposited at 300

TABLE 4: The Effect of Deposition Temperature on the Number of Nitrogen and Carbon Atoms and Calculated C/N Ratios (Obtained from Elemental Analyses) of Gas-Phase-Deposited Aminopropylalkoxysilanes on Silica

deposition temperature/°C	nitrogen atoms/nm^2 of silica (pretreated at 600 °C)			carbon atoms/nm^2 of silica (pretreated at 600 °C)			C/N ratio (pretreatment temp of silica in brackets/°C)		
	APTS	APTM S	APDM S	APTS	APTMS	APDMS	APTS	APTMS	APDMS
125			1.4			6.9			4.9
150	1.6	1.3	1.6	7.6	7.1	6.9	3.7 (200)	4.3^b (200)	3.8 (200)
							3.9 (450)	4.6^b (450)	3.5 (450)
								5.3^b (600)	
								5.2^b (800)	
							4.6 (600)		4.4 (600)
							4.2 (800)		4.8 (800)
200	1.3		1.3	6.4		5.9	4.9		4.5
250		1.3			4.6			3.5	
300	0.76−1.2^a		1.2	3.3−5.3^a		4.9			4.1

[a] Results for elemental analyses have deviation because of the decomposition reactions. [b] Samples not characterized by solid-state NMR.
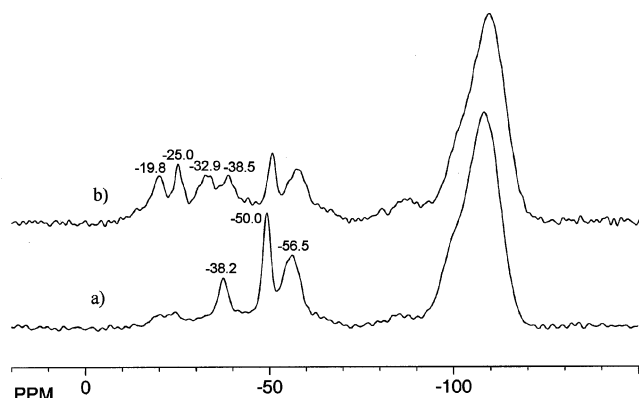
Figure 2. ^{29}Si CP/MAS NMR spectra (measured with equipment A) of APTMS deposited onto silica pretreated at 600 °C at reaction temperatures of (a) 150 °C (16 000 scans) and (b) 250 °C (15 000 scans).
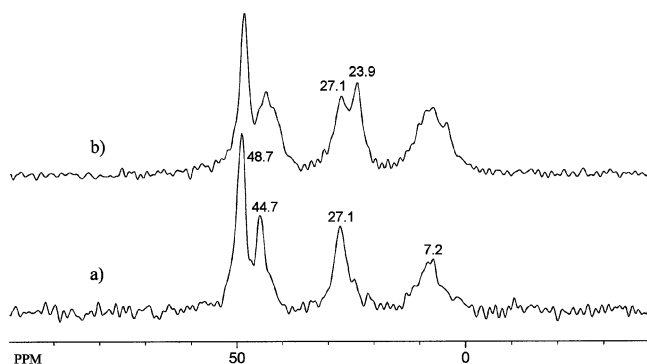

Figure 3. ^{13}C CP/MAS NMR spectra (measured with equipment A) of APTMS deposited onto silica pretreated at 600 °C at reaction temperatures of (a) 150 °C (2000 scans) and (b) 250 °C (12 000 scans).

°C on silica indicating decomposition of ethoxy groups and other surface structures on silica. The existence of OH groups on the surface was also observed through ^{1}H MAS NMR measurements. The variation in the elemental concentrations of samples deposited at high temperatures also supports the assumption that decomposition of aminopropylsilanes on silica occurs. At deposition temperatures higher than 150 °C, the deposition on silica is no longer surface-controlled ALD-type growth.

3.1.2. APTMS Deposited at 150 and 250 °C on Silica Heat-Treated at 600 °C. APTMS was observed to react at 150 °C with the silica surface as APTS forming mono- and bidentately bound surface structures (Chart 2, Table 2, Figure 2). The amino group moiety of APTMS molecules was also observed to react with the silica surface at 150 °C because a strong peak at −39 ppm was observed in the ^{29}Si CP/MAS NMR spectrum (Figure 2a, Chart 3). At the same region, the silicon atoms of liquid APTMS molecules are observed (Table 2). At the higher deposition temperature, 250 °C, a group of new bands appeared at −33, −25, and −20 ppm (Figure 2b) which was only faintly seen at 150 °C. In addition to the reaction with the methoxy groups, the amino groups of APTMS molecules react with the silanols because O$_3$−Si−N− species are observed approximately from −80 to −90 ppm at both deposition temperatures. The reactions of the amino group also cause splitting of the peaks for the carbons in the propyl chain, as seen in the ^{13}C NMR spectrum in Figure 3b. The chemical shifts of the peaks in the ^{13}C CP/MAS NMR spectra will further be discussed in section 3.3. In contrast to APTS, the surface density of nitrogen atoms of APTMS on silica stays constant, namely, at 1.3 molecules/nm^2 (Table 4), when the deposition temperature is increased from 150 to 250 °C. However, at the same time, a
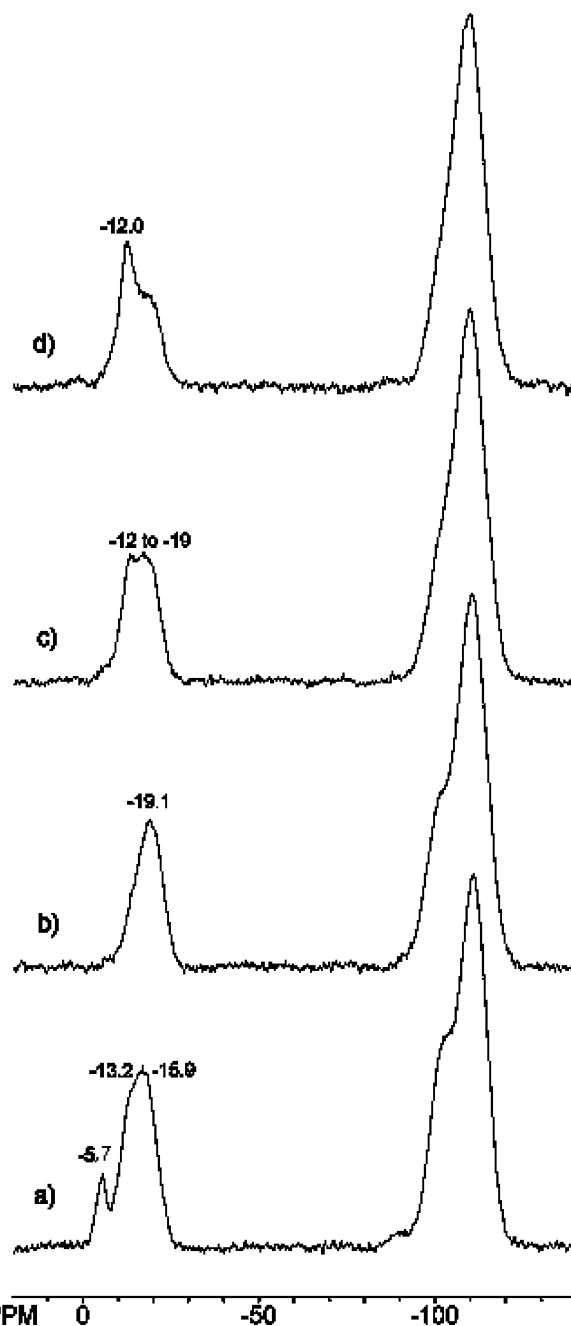

Figure 4. ^{29}Si CP/MAS NMR spectra (measured with equipment B) of APDMS deposited onto silica pretreated at (a) 200 °C, (b) 450 °C, (c) 600 °C, and (d) 800 °C at a reaction temperature of 150 °C (16 000 scans).

diminishment in the number of carbon atoms from 7.1 atoms/ nm^2 to 4.6 atoms/ nm^2 is observed. Thus, consequently the carbon/nitrogen ratio is also decreased from 5.5 to 3.5.

3.1.3. APDMS Deposited at 125−300 °C on Silica Heat-Treated at Various Temperatures. APDMS molecules were observed to react from the gas phase at 150 °C both mono- and bidentately on silica heat-treated at 600 °C. Mono- and bidentate bonding modes were observed as chemical shifts from −12 to −13 and from −17 to −19 ppm in the ^{29}Si NMR spectrum (Figure 4, Chart 4, Table 2). The use of a lower deposition temperature, 125 °C, resulted in a somewhat lower surface density of nitrogen and carbon atoms so the highest coverage of amino groups on the silica surface could be obtained near the temperature of 150 °C. The use of higher deposition temperatures, namely, 200 and 300 °C, resulted in a distinct
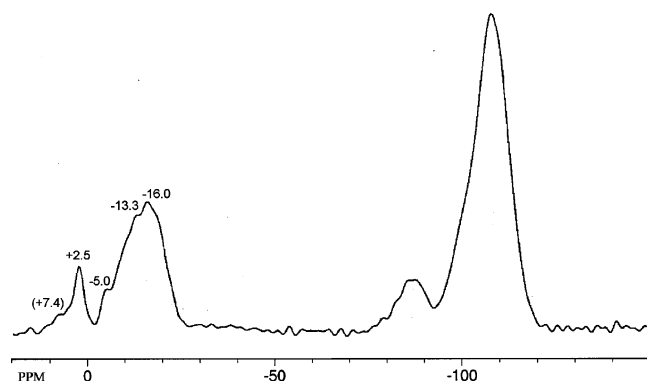
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Figure 5. A ^{29}Si CP/MAS NMR spectrum (measured with equipment A) of APDMS deposited onto silica pretreated at 600 °C at a reaction temperature of 300 °C (17 000 scans).
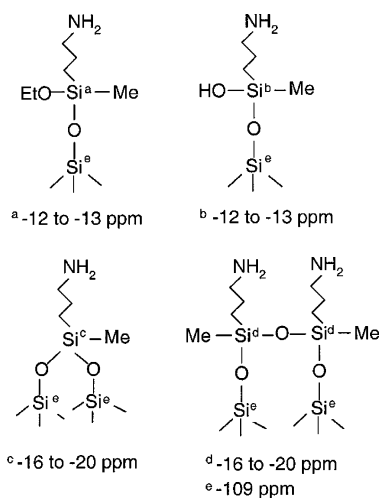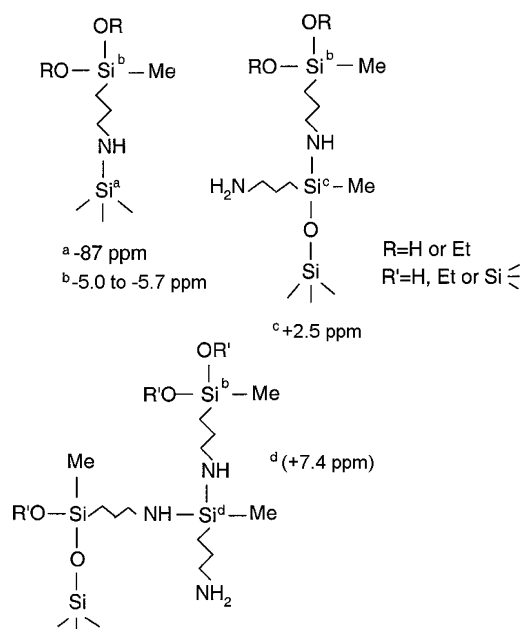
CHART 4

CHART 5

Figure 6. ^{13}C CP/MAS NMR spectra (measured with equipment B) of APTS deposited onto silica pretreated at (a) 200 °C, (b) 450 °C, (c) 600 °C, and (d) 800 °C at a reaction temperature of 150 °C (14 000 scans).

diminishment of the number of nitrogen and carbon atoms on silica, as was observed for APTS.

According to ^{29}Si CP/MAS NMR (Figure 4), the amino groups of APDMS molecules were observed to react at 150 °C only on silica pretreated at 200 °C. This was seen as a new peak at −5.7 ppm (Chart 5). At the same spectral position, a
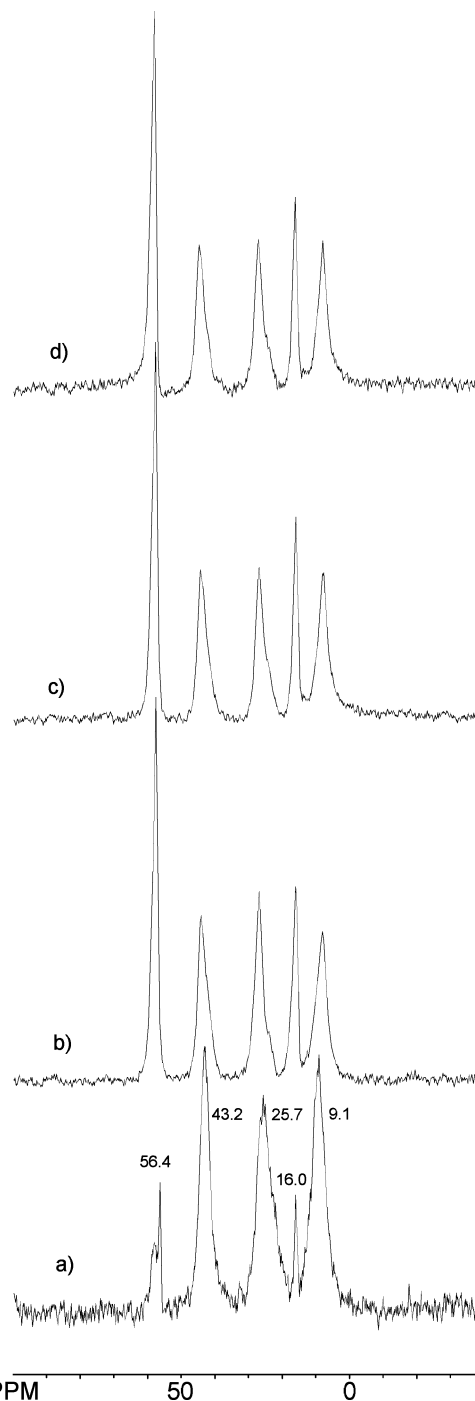
peak for the silicon atoms of liquid APDMS molecules can be seen (Table 2). The reaction of the amino groups with the silanols of silica and the ethoxy groups of APDMS molecules was observed to take place to a larger extent when the deposition temperature was increased to 300 °C. This can be seen as an increase in the intensity of the peak at about −5.0 ppm and the broad peak due to O_3−Si−N surface species approximately at −90 ppm and additionally an appearance of peaks at +2.5 and +7.4 ppm (Figure 5). Because the last-mentioned peak is very weak, only a very small number of surface species shown in Chart 5d is likely to exist. It was expected because only very few free ethoxy groups exist on the surface which could further react with the amino groups.
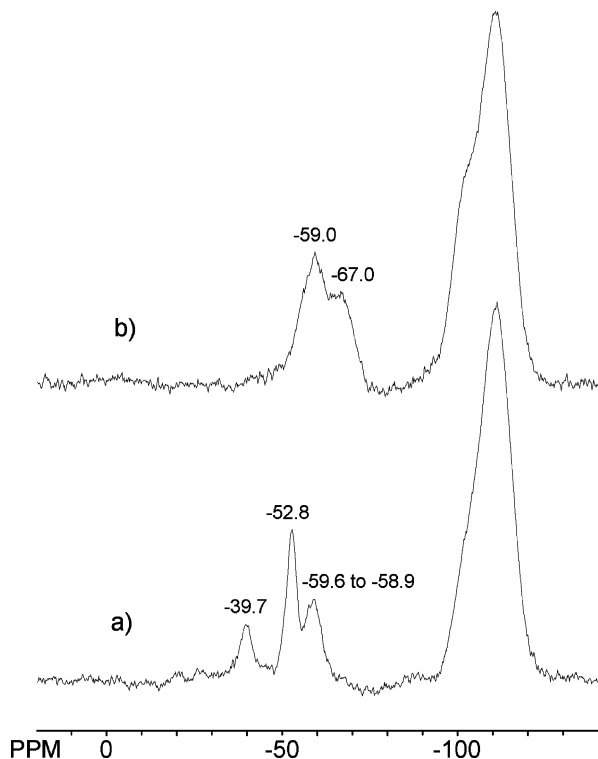
Figure 7. ^{29}Si CP/MAS NMR spectra (measured with equipment B) of APTS on silica (pretreated at 450 °C) (a) before and (b) after treatment with water at 200 °C (16 000 scans).

3.2. Hydrolysis of Aminosilylated Silica Samples.

Aminopropylalkoxysilane precursors and aminosilylated silica samples are sensitive to hydrolysis. During the deposition process, traces of water were excluded because of the use of elevated temperatures and reduced pressure. As expected, according to our ^{29}Si NMR results no hydrolyzed species of ethoxy groups of APTS molecules were observed on silylated silica surface when the deposition was performed at 150 °C (Figure 1). Also, the ^{13}C NMR data (Figure 6b) shows that there are still lots of ethoxy groups present on the surface. However, hydrolysis of ethoxy groups was probably observed at higher deposition temperatures as chemical shifts below −50 ppm, as was discussed above. In the liquid-phase studies, the hydrolyzed surface species of monodentately bound APTS on silica are observed in the region of 43−49 ppm in the exact chemical shift depending on the study.[1,9,12−13] However, hydrolyzed surface species of bidentately bound APTS molecules cannot be distinguished from the unhydrolyzed ones by ^{29}Si NMR (Chart 2d and 2e).[9]

According to our previous DRIFTS study, a water treatment of APTS-derivatized silica at 200 °C resulted in a complete disappearance of ethoxy groups and formation of hydroxyl groups instead.[4] The ^{29}Si CP/MAS NMR spectra of APTS on silica, pretreated at 450 °C, before and after hydrolysis at 200 °C in the gas phase are shown in Figure 7. After water treatment, no monodentately bound surface species with or without hydrolyzed ethoxy groups at about −50 ppm were unexpectedly observed on the surface but both bi- and tridentate surface species were seen at −59 and −67 ppm, respectively. It seems that the hydrolyzed alkoxy groups have reacted forming siloxane bridges because of the occurring cross-linking reactions. A decrease in the number of monodentate linkages and the increase of bi- and tridentate linkages because of cross-linking reactions have also been observed in a liquid-phase study where silica gel pretreated at 190 °C was modified with APTS in toluene,
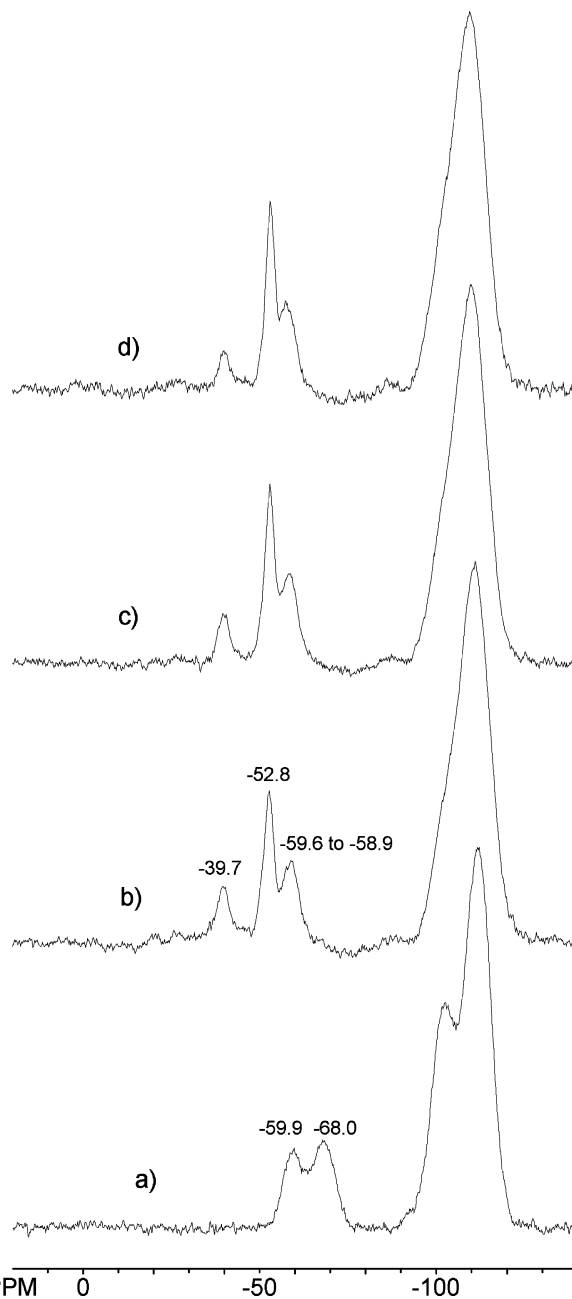

Figure 8. ^{29}Si CP/MAS NMR spectra (measured with equipment B) of APTS deposited onto silica pretreated at (a) 200 °C, (b) 450 °C, (c) 600 °C, and (d) 800 °C at a reaction temperature of 150 °C (16 000 scans).

first heat-treated at 200 °C, and then treated with water.[9] The peak below −50 ppm also cannot be observed after the water treatment according to the same literature study. The various forms of tridentately bound surface species seen at −67 ppm are shown in Chart 2f−h. When the ^{29}Si NMR spectra of APTS on silica before and after the water treatment are compared (Figure 7a and 7b), the peak at −40 ppm is observed to disappear. Thus, the surface species shown in Chart 3b are observed to vanish after water treatment. This can be explained by the scission of the silicon−nitrogen bonds which are generally known to be extremely sensitive to hydrolysis.

3.3. Effect of Pretreatment Temperature of Silica on the Bonding Modes of APTS, APTMS, and APDMS on the Surface when the Precursors Were Deposited at 150 °C.

As shown above, both elemental analyses and ^{29}Si CP/MAS NMR spectroscopy can be exploited for the determination of the

A ^{29}Si and ^{13}C CP/MAS NMR Study

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TABLE 5: ^{13}C CP/MAS NMR Results of APTS and APDMS (and APTMS) Deposited on Heat-Treated Silica at 150 °C and Literature Results from the Gas- and Liquid-Phase Studies

aminosilane	ref	pretreatment of silica/°C	Chemical shifts/ppm						
			−C(3)H₂−NH₂	−C(2)H₂−	−C(1)H₂−Si-	−OCH₂−	−CH₂−CH₃	−OCH₃	−CH₃−Si
APTS		200	43.2	25.7	9.1	56.4	16.0		
APTS		450	44.0−44.2	26.5−27.0	8.1−8.7	57.6−57.7	15.9−16.1		
APTS		600	43.4−44.3	26.6−26.9	7.7−8.7	57.7−57.8	15.8−15.9		
APTS		800	42.9−44.5	25.2−26.8	7.7−8.4	57.7−58.5	15.6−15.9		
APTS	6	450	44	27	9	58	16		
APTS	11	200	43	21-27	10	56	17		
APTS [a]	10		45.2	27.4	7.9	58.3	18.4		
APD MS		200	44.4−44.8	26.9−27.3	13.1−13.5	57.3−57.9	16.6[b]		−2.9 to −3.8
APD MS		450	44.0	26.5	13.0	(57.9 w)	[b]		−4.1
APD MS		600	44.7	26.8	12.7	57.6	[b]		−4.2
APD MS		800	44.6	26.6	12.6	57.4	15.6[b]		−4.4
APT MS		600	44.7	27.1	7.2			48.7	
APT MS [a]	29		45.3	28.0	6.5			50.8	

[a] Liquid-phase NMR results of pure precursor. [b] Only a very weak shoulder is observed.

bonding modes of aminopropylalkoxysilanes on the silica surface. However, the determined carbon/nitrogen ratio gives only a rough indication of bonding modes and more detailed information on the bonding modes and structure of the surface species can be obtained by ^{29}Si NMR. The bonding modes of aminopropylalkoxysilanes were studied on silica pretreated at various temperatures and deposited at 150 °C.

3.3.1. APTS on Silica. According to the calculated carbon/nitrogen ratios, namely, 3.7−4.6 (Table 4), APTS molecules seem to be mainly bound both bi- and tridentately regardless of the pretreatment temperature of silica (200−800 °C).[2] However, according to the ^{29}Si NMR results (Table 2 and Figure 8), bi- and tridentate bonding modes were observed only on silica pretreated at 200 °C. When silica pretreated at 190 °C has been modified with APTS in toluene, mono- and bidentate bonding modes were observed by ^{29}Si NMR to coexist on the surface.[9] However, subsequent heating at 200 °C enabled cross-linking reactions to occur whereupon the number of monodentate structures decreased, and the number of bidentate structures increased, but at the same time tridentately bound surface species were generated on the surface.[9] In our study at higher pretreatment temperatures of silica, that is, at 450−800 °C, both mono- and bidentate bonding modes of APTS were observed on silica. It can be observed on the basis of C/N ratios (Table 4) that APTS is bound through fewer ethoxy ligands with silanols when the heat-treatment temperature is raised from 200 to 600 °C. In the liquid-phase studies, the number of tridentate surface structures of APTS on silica has been observed to decrease compared to the number of bidentate structures when the pretreatment temperature of silica is increased from 200 to 700 °C.[12]

The sharp peaks in the solid-state ^{13}C NMR spectra of APTS on silica (Figure 6) indicate well-ordered surface structures on the silica surface. There are five signals in the ^{13}C CP/MAS NMR spectrum of APTS on silica when the precursor molecules are bound mono- or bidentately. The chemical shifts based on previous studies[6,11] of APTS on silica as well as liquid-phase ^{13}C NMR results[10] of liquid APTS are shown in Table 5. Two signals of unreacted ethoxy groups are located at 16 and 58 ppm and three signals due to propyl spacer ($H_2N−CH_2(3)−CH_2(2)−CH_2(1)−Si$) at 44 (C3), 27 (C2), and 9 (C1) ppm have been observed in the previous gas-phase studies.[4,6] In our study, the carbon atom of the methyl group is observed at about 16 ppm and the carbon of −OCH₂− group at 56−58 ppm, while the carbon atoms in the propyl chain are seen at 43−44, 26−27, and 8−9 ppm (Figure 6). When the number of bi- and tridentate surface species of APTS on silica increases, the relative intensity of two signals due to ethoxy groups (16 and

56−58 ppm) decreases. This can very clearly be seen when the aminosilylated silica samples pretreated at 200 and 800 °C are compared.

3.3.2. APTMS on Silica. According to the present ^{29}Si NMR results (Figure 2), it can be concluded that APTMS is both mono- and bidentately bound on silica pretreated 600 °C. According to the calculated carbon/nitrogen ratios, that is, 5.3 (Table 4), APTMS molecules seem to be mainly monodentately bound. The bonding mode of APTMS was determined by means of ^{29}Si NMR only on silica pretreated at 600 °C. However, according to the calculated C/N ratios, a larger number of bidentately bound APTMS molecules was observed at low pretreatment temperatures of silica (200−450 °C) while a larger number of monodentately bound APTMS was found at high pretreatment temperatures of silica (600−800 °C). Thus, APTMS and APTS seem to chemically behave in a similar way on silica.

When APTMS is bound on the silica surface, the chemical shifts of the carbon atoms of −CH₂− groups are seen at 44.7 (C3), 27.1 (C2), and 7.2 ppm (C1) and the carbon of the −OCH₃ group at 48.7 ppm (Figure 3, Table 5) in the ^{13}C CP/MAS NMR spectra. For comparison, the chemical shifts of carbon atoms for liquid APTMS are tabulated in Table 5. At a higher deposition temperature, namely, 250 °C, the carbon atoms C3, C2, C1, and −OCH₃ were observed at 43.9, 27.1 and 23.9, 7.5, and 48.6 ppm, respectively. The largest difference was observed in the C2 peak which has become broader and split into two. At the same time, the peaks for C3 and C1 were shifted to higher fields and lower fields, respectively. As a matter of fact, the peaks corresponding to the first and third carbon in the propyl chain were also observed to split. This is due to the surface species involved in the reaction of the amino group moiety of the molecule causing the carbon atoms to exist in two different chemical environments. A slight broadening of the C2 peak has also been observed in the liquid-phase study where APTS in an organic solvent was deposited on silica, treated at 200 °C, and further treated with water.[9] In the same study, a broad peak in the ^{29}Si NMR spectrum from −80 to −90 ppm could also be distinguished. On the other hand, a large upfield shift of the C2 carbon has been observed when APTS was hydrolyzed in aqueous solution and deposited on silica and further heat-treated at 130 °C.[18] This is due to the chemical interactions occurring with the amino groups.[11]

3.3.3. APDMS on Silica. According to the elemental analyses, APDMS is mainly bidentately bound on silica pretreated at 200 and 450 °C because the observed C/N ratios are in the range of 3.5−3.8 (Table 4). According to the solid-state ^{29}Si NMR, the

silica surface heat-treated at 450 °C is solely covered with bidentate species of APDMS because only one band at −19.1 ppm is seen in the spectrum (Figure 4b and Table 2). In addition, the ^{13}C NMR results support this conclusion because only a very faint peak due to methylene of ethoxy groups at 57.9 ppm can be observed. However, APDMS is bound on silica heat-treated at 200 °C both in a mono- and bidentate fashion because the chemical shifts are seen at −13.2 and −15.9 ppm in the ^{29}Si NMR spectrum, respectively.

The ^{13}C CP/MAS NMR spectrum of APDMS-modified silica pretreated at 200 °C consists of small peaks at 57.9 and 16.6 ppm which indicates that a small number of methylene groups of ethoxy groups exist (Figure 9). Thus, only a small number of monodentately bound surface species of APDMS exist on silica. Nevertheless, as discussed previously in section 3.1.3., in addition to the above-mentioned peaks a single peak situated at less-negative values at −5.7 ppm seems to be due to the reaction of amino groups with the silanols of silica. This can only be observed on the silica surface pretreated at 200 °C. All chemical shifts in the solid-state ^{29}Si and ^{13}C NMR spectra of APDMS on silica are shown in Tables 2 and 5. In the ^{13}C NMR spectra of APDMS on silica, three signals due to propyl spacer (H_2N−$CH_2(3)$−$CH_2(2)$−$CH_2(1)$−Si) are observed at 44.0−44.8 (C3), 26.5−27.3 (C2), and −2.9−(−4.4) (C1) ppm. Two signals of unreacted ethoxy groups are seen at 57.3−57.9 ppm (methylene) and 16.6 ppm (methyl). In addition, the silicon bound methyl groups are seen at 12.6−13.5 ppm. When APDMS has been used for the modification of silica in the liquid phase and the sample was cured in air, the relative contributions of mono- and bidentate forms were 10 and 90%, respectively.[1]

APDMS molecules seem to be bound on silica, pretreated at higher temperatures, 600 and 800 °C, both in a mono- and bidentate fashion on the basis of calculated C/N ratios, namely, 4.4−4.8. Broad peaks are observed from about −5 to −25 ppm in the ^{29}Si CP/MAS NMR spectra where two separate peaks corresponding to mono- and bidentate bonding modes can be distinguished. The relative number of monodentately bound surface species compared to the number of bidentately bound species is likely to increase when the pretreatment temperature of silica is increased from 600 to 800 °C. This is seen as a separation of a sharper peak at −12.0 ppm in the middle of the above-mentioned broad band. According to the elemental analyses, the C/N ratio increases when the pretreatment temperature of silica is increased from 200 to 800 °C. Thus, the number of surface species bound in a monodentate fashion obviously increases when the pretreatment temperature of silica is increased. All possible bonding modes of APDMS on silica, when deposited via the gas phase, are shown in Charts 4 and 5.

4. Conclusions

The surface species and bonding modes of gas-phase-deposited aminopropylalkoxysilanes, APTS and APDMS, and to a lesser degree also APTMS, were successfully studied by ^{29}Si and ^{13}C CP/MAS NMR spectroscopies. Dehydroxylation state of silica and especially the deposition temperature had a distinct effect on the bonding modes of the studied aminopropylalkoxysilanes on silica. For the deposition of aminosilanes on silica, a deposition temperature equal to or less than 150 °C should be used to avoid the secondary reactions of amino groups on the silica surface. At 150−300 °C, the amino groups of trifunctional APTS and APTMS were observed to react both with the alkoxy groups of other precursor molecules and silanols of silica. These reactions of amino groups on silica were not observed with bifunctional APDMS on silica pretreated at 450−
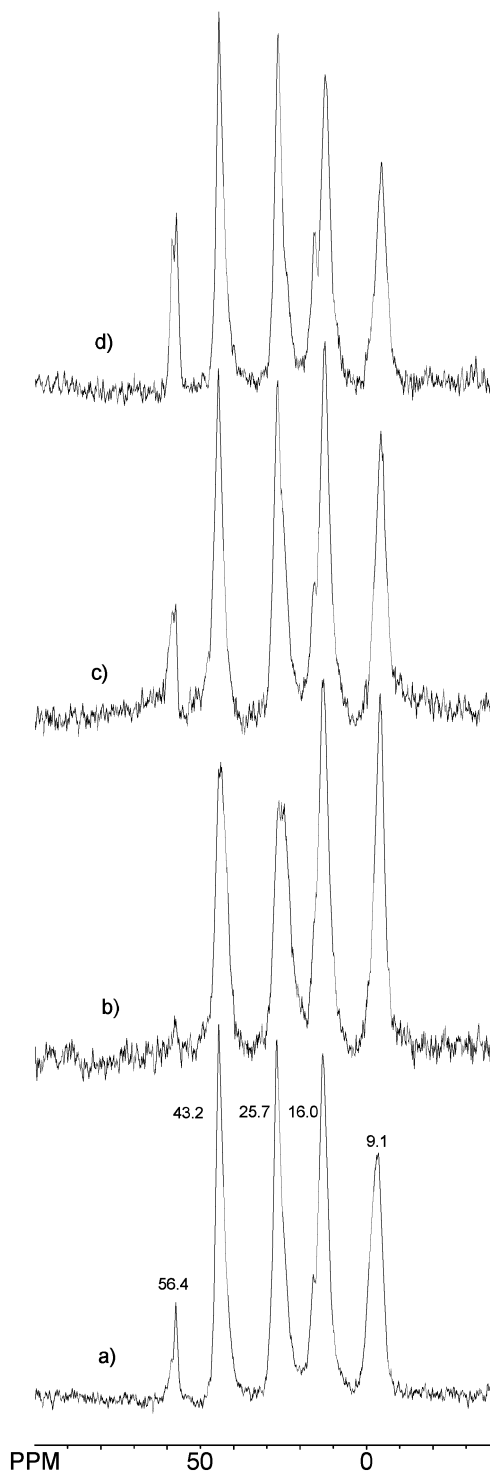

Figure 9. ^{13}C CP/MAS NMR spectra (measured with equipment B) of APDMS deposited onto silica pretreated at (a) 200 °C, (b) 450 °C, (c) 600 °C, and (d) 800 °C at a reaction temperature of 150 °C (14 000 scans).

800 °C at the deposition temperature of 150 °C but the amino groups were observed to react when the temperature was raised to 300 °C. However, the amino groups of APDMS molecules were observed to react on the surface when silica was pretreated at 200 °C.

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