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# CONTROLLED PREPARATION OF AMINO-FUNCTIONALIZED SURFACES ON POROUS SILICA BY ATOMIC LAYER DEPOSITION

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# CONTROLLED PREPARATION OF AMINO-FUNCTIONALIZED SURFACES ON POROUS SILICA BY ATOMIC LAYER DEPOSITION

Satu Ek (*née* Härkönen)

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Chemical Technology for public examination and debate in Auditorium KE 1 at Helsinki University of Technology (Espoo, Finland) on the 11th of December, 2004, at 12 noon.

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**ABSTRACT**

The aim of the research was to study the preparation of amino-functionalized silicon dioxide surfaces from the gas-phase by atomic layer deposition (ALD) technique. ALD and other gas-phase techniques have rarely been used for the deposition of organic precursors, in this case various γ-aminopropylalkoxysilanes. Thermogravimetry (TG) and diffuse reflectance infrared Fourier spectroscopy (DRIFTS) with multivariate calibration, i.e. projections to latent structures by means of partial least squares (PLS), were applied for the first time to study of the surface species on various porous silicon dioxide, i.e. silica, samples. The gas-solid reactions of aminopropylalkoxysilane precursors on porous silica were investigated at various deposition temperatures by depositing a single surface-saturated molecular layer of precursors by ALD. Study was also made of the effects of pretreatment temperature of silica and type of precursor, and the effect of using sequential aminopropylalkoxysilane/water cycles on the surface density of amino groups on silica. As an example of the growth of organic multilayered structures on aminosilylated silica, the deposition of polyimide structures was demonstrated. The basic principles of ALD on porous substrates and a review of the literature on the use of silanes in gas-phase processes are presented by way of background.

The study showed TG to be a simple and relatively fast technique for determination of the total number of silanol groups on silica. Combined DRIFTS/PLS procedure also enabled fast determination of the total number of silanols after calibration with the results from TG measurements. Separate determination of the different types of silanols was not possible with these methods, however. For reference and practical purposes, the numbers of isolated and hydrogen-bonded silanols were also determined by $^{1}H$ MAS (magic angle spinning) NMR, but this is a slower and more expensive technique.

Trifunctional γ-aminopropyltrimethoxysilane (APTMS), γ-aminopropyltriethoxysilane (APTS), and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPS); bifunctional γ-aminopropyldiethoxymethylsilane (APDMS); and monofunctional γ-aminopropyldimethyl-ethoxysilane (APDMES) were used as precursors for the deposition of amino-functionalized surfaces on silica. The aminosilylated silica surfaces were characterized by DRIFTS, solid-state $^{29}Si$ and $^{13}C$ nuclear magnetic resonance (NMR), and elemental analyses.

According to the results, homogeneous aminosilylated silica surfaces can be prepared by ALD at low temperatures (≤ 150 °C) in a reproducible way by a solvent-free procedure. The deposition of a single surface-saturated molecular layer on silica led to densities between 1.0 and 2.1 amino groups/nm$^2$ depending on the pretreatment temperature of silica (200-800 °C) and the precursor. The highest amino group density was achieved with the bifunctional precursor, APDMS, on silica pretreated at 200 °C. The use of relatively high deposition temperatures, i.e. 150-300 °C, led to side-reactions between the amino groups of bi- and trifunctional precursors and silanol groups or alkoxy groups of other precursor molecules on silica. The amino group density could be better controlled when sequential reactions of trifunctional aminopropylalkoxysilanes and water were applied. Thus, depending on the number of APTS/-, APTMS/-, or AAPS/water cycles, surface densities from 1.5-1.9 to 2.8-3.0 terminal amino groups/nm$^2$ were achieved. After four cycles the surface was saturated and a constant surface density of nitrogen and carbon atoms was achieved. The deposition of a monolayer on the surface was thus achieved.

**PREFACE**

The experimental work of this thesis was carried out in the Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, between May 1998 and December 2003.

I wish to express my deep gratitude to my supervisor Prof. Lauri Niinistö and my advisor Dr. Eero Iiskola for their continuous support and encouragement during this work, especially during the past few years. I greatly appreciate the expert supervision of Dr. Eero Iiskola and his contribution to my research. His enthusiasm and genuine interest motivated me to carry on with my studies. I wish to thank Prof. Lauri Niinistö for his expert help and advice, especially in the preparation of the manuscripts.

My co-authors provided a fruitful co-operation and valued expertise; Dr. Andrew Root, Prof. Tuula Pakkanen, and Mr. Jari Vaittinen measured the solid-state NMR spectra and contributed to the interpretation of the NMR results; Mr. Marko Peussa lent his expertise in the multivariate analysis; Dr. Jetta Keränen, Prof. Aline Auroux, and Mr. Janne Puputti assisted in the characterization of numerous silica samples; Dr. Minna Nieminen provided kind and expert help and advice, especially in the finalizing of this manuscript; Ms. Hanna Salmio assisted in some of the ALD experiments; and indeed, the entire personnel of the Laboratory of Inorganic and Analytical Chemistry were generous in their practical advice and support. I am deeply grateful to you all. Dr. Kathleen Ahonen is thanked for revising the language of this thesis.

Financial support from the Fortum Foundation, Helsinki University of Technology, Jenny and Antti Wihuri Foundation, the Academy of Finland, the Finnish Foundation of Technology, the Graduate School of Inorganic Material Chemistry and the Association of Finnish Chemical Societies is gratefully acknowledged. I am also grateful to my present employer, Preseco Oy, for the positive attitude and support enabling me to complete this thesis.

Finally, I warmly thank my dear family Janne and Patrik, my mother Kaarina, my grandmother Linnea, as well as my friends for their empathy and support. Special thanks go to my mother- and father-in-law for taking care of Patrik during the busy summer of 2004.

Espoo, November 2004

Satu Ek

**LIST OF PUBLICATIONS**

In addition to the present review, the dissertation includes the following publications, which are referred to in the text by the corresponding Roman numerals:

I Ek, S., Root, A., Peussa, M., Niinistö, L., Determination of the hydroxyl group content in silica by thermogravimetry and a comparison with $^{1}H$ MAS NMR results, *Thermochim. Acta* **379** (2001) 201-212.

II Peussa, M., Härkönen, S., Puputti, J., Niinistö, L., Application of PLS multivariate calibration for the determination of hydroxyl group content in silica by DRIFTS, *J. Chemom.* **14** (2000) 501-512.

III Ek, S., Iiskola, E.I., Niinistö, L., Gas-phase deposition of aminopropylalkoxysilanes on porous silica, *Langmuir* **19** (2003) 3461-3471.

IV Ek, S., Iiskola, E.I., Niinistö, L., Pakkanen, T.T., Root, A., New bonding modes of gas-phase deposited γ-aminopropyltriethoxysilane on silica studied by $^{29}Si$ CP/MAS NMR, *Chem. Commun.* (2003) 2032-2033.

V Ek, S., Iiskola, E.I., Niinistö, L., Vaittinen, J., Pakkanen, T.T., Root, A., A $^{13}C$ and $^{29}Si$ CP/MAS NMR study of bi- and trifunctional γ-aminopropylalkoxysilanes deposited onto porous silica in the gas phase, *J. Phys. Chem. B* **108** (2004) 11454-11463.

VI Ek, S., Iiskola, E.I., Niinistö, L., Vaittinen, J., Pakkanen, T.T., Keränen, J., Auroux, A., Atomic layer deposition of amino-terminated siloxane network on silica through sequential reactions of γ-aminopropyltrialkoxysilanes and water, *Langmuir* **19** (2003) 10601-10609.

VII Ek, S., Iiskola, E.I., Niinistö, L., Atomic layer deposition of amino-functionalized silica surfaces using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane as a silylating agent, *J. Phys. Chem. B* **108** (2004) 9650-9655.

Besides the findings reported in publications I-VII, the present manuscript summarizes some new results on the atomic layer deposition of organic multilayered, i.e. polyimide, structures on amino-functionalized silica surface.

## THE AUTHOR'S CONTRIBUTION TO THE APPENDED PUBLICATIONS

| | |
|---|---|
| Publication I | The author defined the research plan for the experimental work together with the co-authors. The author carried out the experimental work, interpreted the results and wrote the manuscript. |
| Publication II | The author carried out the TG and DRIFTS measurements. Interpretation of the results and writing of the manuscript was done together with Mr. Marko Peussa. |
| Publications III and VII | The author defined the research plan and interpreted the results with Dr. Eero Iiskola. The atomic layer depositions and the measurements of the DRIFT spectra were performed by the author. Both manuscripts were written by the author. |
| Publications IV and V | The author defined the research plan together with Dr. Eero Iiskola, deposited the aminosilylated silica samples and interpreted the results with the co-authors. The author wrote the manuscripts. |
| Publication VI | The author defined the research plan together with Dr. Eero Iiskola, prepared the aminosilylated silica samples, carried out the DRIFTS measurements and interpreted the results with the co-authors. The author also wrote the article. |

## LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| AAPS | N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane |
| ALCVD | Atomic Layer Chemical Vapor Deposition |
| ALD | Atomic Layer Deposition |
| ALE | Atomic Layer Epitaxy |
| ALG | Atomic Layer Growth |
| APDMES | γ-Aminopropylethoxydimethylsilane |
| APDMS | γ-Aminopropyldiethoxymethylsilane |
| APTMS | γ-Aminopropyltrimethoxysilane |
| APTS | γ-Aminopropyltriethoxysilane |
| BDMADMS | Bis(dimethylamino)dimethylsilane |
| BET | Brunauer-Emmett-Teller |
| CP | Cross Polarization |
| CRAMPS | Combined Rotation And Multiple Pulse Spectroscopy |
| CVD | Chemical Vapor Deposition |
| DAH | Diaminohexane |
| DLE | Digital Layer Epitaxy |
| DMCSE | 1-(Dimethylchlorosilyl)-2-(p, m-chloromethylphenyl)ethane |
| DMDM | Dimethyldimethoxysilane |
| DTA | Differential Thermal Analysis |
| DTG | Derivative of the TG curve |
| DRIFT/S | Diffuse Reflectance Fourier Transform Infrared /Spectroscopy |
| FTIR | Fourier Transform Infrared |
| HFTS | Heptadecafluorodecyltrichlorosilane |
| HMDS | 1,1,1,3,3,3-Hexamethyldisilazane, $(CH_3)_3$-Si-NH-Si-$(CH_3)_3$ |
| IR | Infrared |
| MAS | Magic Angle Spinning |
| MDD | Molecular Designed Dispersion |
| MDMS | Methyldimethoxysilane |
| MLD | Molecular Layer Deposition |
| MLE | Molecular Layer Epitaxy |
| MPTMS | 3-Mercaptopropyltrimethoxysilane |

| | |
|---|---|
| MTES | Methyltriethoxysilane |
| MTMS | Methyltrimethoxysilane |
| NFTS | Nonafluorohexyltrichlorosilane |
| NMR | Nuclear Magnetic Resonance spectroscopy |
| OSC | Orthogonal Signal Correction |
| PLS | Projections to Latent Structures by means of Partial Least Squares |
| PMDA | Pyromellitic dianhydride, 1,2,3,5-benzenetetracarboxylic anhydride |
| RMSEP | Root Mean Squared Error of Prediction |
| TA | Thermal Analysis, thermoanalytical |
| TDMCS | p-Tolyldimethylchlorosilane |
| TEA | Triethylamine |
| TEOS | Tetraethoxysilane |
| TES | Triethylsilanol |
| TFTS | Trifluoropropyltrichlorosilane |
| TG | Thermogravimetry |
| TMCS | Trichloromethylsilane |
| TMES | Trimethylethoxysilane |
| TMMS | Trimethylmonomethoxysilane |
| TMOS | Tetramethoxysilane |
| TMSCl | Tris(trimethylsiloxy)chlorosilane |

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# 1. INTRODUCTION

There is growing interest in the use of organic molecular overlayers on solid surfaces for a variety of applications. Amino-functionalized surfaces can be obtained by binding simple compounds bearing an amine group, e.g. γ-aminopropylalkoxysilanes, onto solid surfaces. Aminopropylalkoxysilanes deposited onto porous or non-porous, amorphous silicon dioxide particles, i.e. silica, or as thin films onto crystalline silicon wafers are widely used as coupling agents to immobilize other ions or molecules on the surface.[1,2] Organic multilayered structures, such as polymeric assemblies, can further be prepared on aminosilylated surfaces by exploiting more complex organic reactions to build multilayered structures with several components.[3,4] Thus, aminopropylalkoxysilanes have wide-spread applications in analytical[5-8] and material chemistry,[9-12] biochemistry,[13-15] catalyst technology,[16-19] and electronics[1,20]. They are applied in chromatographic columns,[5,6] in the concentration of metals,[7,8] in the adhesion of polymers,[9] metals[12] and biochemical molecules[13-15] to surfaces, in the corrosion protection of metals,[10,11] and for the construction of nanoscale chemical patterns[20].

Despite the widespread use of these materials, the preparation of well-defined amino-functionalized surfaces is not straightforward.[21] The preparative route to silylated silicon dioxide surfaces has a major effect on the quality of the product.[1] Especially with alkoxysilanes, the presence of water has a significant influence on the mechanism of molecular layer formation and thereby on the structure of the deposited layer. Thus, the preparation of silylated silica surfaces from the liquid phase, i.e. in aqueous ambient or an organic solvent, results in uncontrolled formation of polymeric multilayers. The preparation of silylated surfaces is nevertheless mostly performed from the liquid phase. For precisely tailored materials, a reproducible method of deposition resulting in a controllable layer thickness or surface density is essential.[22] In chromatographic columns, for example, problems such as peak tailing originate from incomplete derivatization, which leaves unreacted silanol groups on the surface.[23]

The gas-phase deposition of silanes on the surface has to some extent been studied for academic and research purposes. However, before this work, there were no fundamental studies on the gas-solid reactions of aminopropylalkoxysilane precursors on porous or non-porous surfaces or on the preparation of amino-functionalized surfaces from the gas phase. Products deposited from the gas phase have nevertheless been observed to possess

significantly improved performance characteristics[6] and to be better-ordered than layers deposited from toluene solutions[24].

The overall objective of this work was to study the use of atomic layer deposition (ALD)[25-27] for the preparation of amino-functionalized surfaces on porous silica from the gas phase. ALD and other gas-phase techniques have rarely been exploited for the deposition of organic layers on porous or non-porous surfaces. ALD has been mainly applied for the preparation of metal oxide, sulfide, and nitride thin films on silicon wafers for electronic applications.[28-35] Metal-containing precursors such as volatile halides and β-diketonate-type chelates or organometallic precursors have been used. With ALD, well-defined surfaces having excellent conformality and large area uniformity can be prepared in a reproducible way on planar,[29] curved,[36] or porous substrates[37]. ALD has been used for the preparation of heterogeneous catalysts where improved and controlled dispersion of the active species was desired.[37-43] ALD also enables study of the formation of overlayers by following the gas-solid reactions step-by-step. A porous, high-surface-area, substrate, such as silica, offers abundant material for chemical characterization.

The characterization of the surface species, i.e. the reactive sites, of the substrate is especially important in ALD because of the surface-controlled nature of the growth. Thermogravimetry (TG) and diffuse reflectance Fourier spectroscopy (DRIFTS) methods for the characterization of the surface species on porous silica were developed and applied for the purpose.[I,II] Study was then focused on the ALD of organic precursors on porous silica surfaces. The effects of the pretreatment temperature of silica and the deposition temperature on the surface density and species formed were studied by depositing a single surface-saturated molecular layer of different γ-aminopropylalkoxysilane precursors on silica.[III-V,VII] In addition, the preparation of a high-density aminopropylsiloxane network was studied by repeated application of sequential aminopropylalkoxysilane/water cycles.[VI,VII] As an example of the growth of organic multilayered structures on aminosilylated silica, the deposition of polyimide structures was demonstrated. The last results are reported here for the first time.

## 2. GENERAL BACKGROUND

As background for the study, liquid- and gas-phase methods used in the preparation of silylated surfaces are reviewed in this chapter. The main emphasis is on the principles and applications of atomic layer deposition (ALD), the gas-phase technique used in the experimental work.

### 2.1 Deposition of silanes onto silicon dioxide surfaces

The method of preparing silylated silicon dioxide surfaces has a significant effect on the layer thickness, surface density, orientation of the surface molecules, and the type of interaction between the surface groups and the precursor molecules.[1] The presence of water significantly affects the mechanism of molecular layer formation and thereby the structure of the deposited layer, especially with alkoxysilanes.

Silylated surfaces are generally prepared by liquid phase methods, i.e. sol-gel, aqueous, or organic solvent methods.[1] The last technique is the most important industrially. In the sol-gel process, functionalized silica is prepared in the liquid phase by adding alkoxysilanes to tetraethoxysilane (TEOS) solution or from the liquid phase by dipping or spinning[44] the material in the silane solution, but this results in a largely irreproducible product where surface density of silanes cannot be precisely controlled. The thickness of the deposited layer is also unpredictable in the aqueous ambient procedure because of uncontrolled condensation reactions (Figure 1). In both cases, thick but irregular multilayers are formed on the surface. Deposition from organic solvents, also called grafting or anchoring, likewise may result in uncontrolled formation of multilayers because, even with careful dehydration treatment, traces of water are always present. The organic solvent techniques involve tedious operations[45], such as solvent removal and recovery, as well as washing procedures, all of which can be avoided by applying gas-phase techniques. There are still other preparative routes to silylated surfaces, for instance a method based on melting of nonvolatile silanes on the substrate[46].

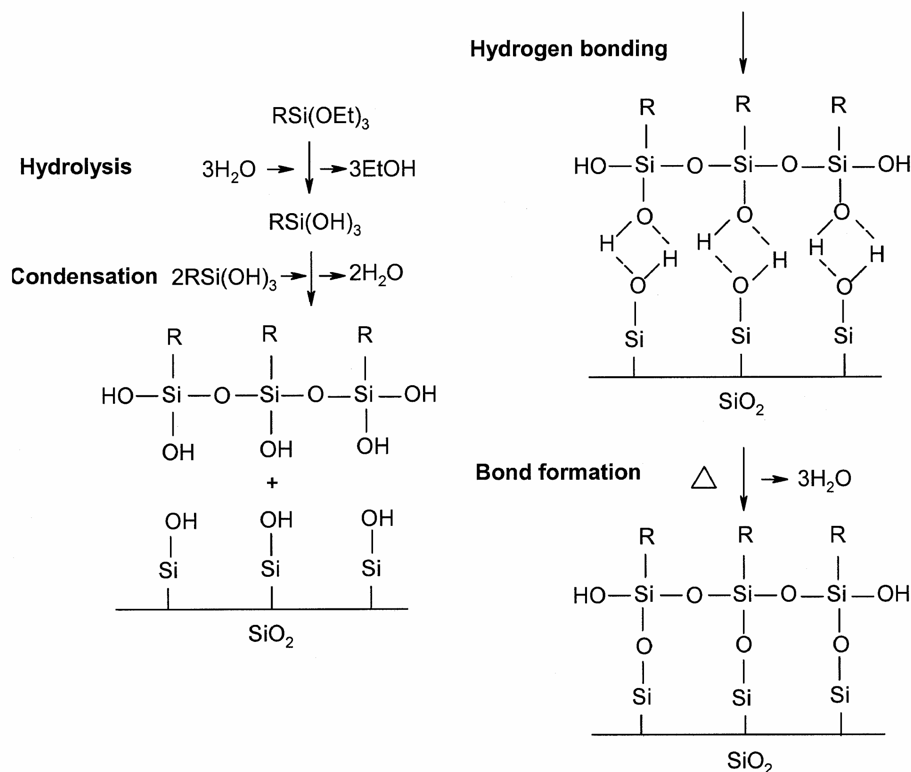



**Figure 1.** Schematic presentation of the reaction sequences when alkoxysilanes are deposited on silica in an aqueous solvent after Vansant et al.[1]

Controlled deposition of surface-saturated molecular layers from the gas phase onto the substrate surface is achieved by vaporizing the precursor molecules and allowing them to react with the substrate under completely dry conditions. The presence of water can be excluded in the gas phase because no solvents are needed and the precursor molecules, which may be possibly hydrolyzed, cannot be vaporized at low deposition temperatures. When alkoxysilanes (or aminoalkoxysilanes) are used as precursors, the hydrolysis of alkoxy groups, hydrogen bonding of hydrolyzed alkoxy groups, and further condensation reactions before deposition can all be avoided (Figure 2).[1] Thus, the chemical interactions of the precursor molecules with the reactive surface species result in direct bond formation and the deposition of a single surface-saturated molecular layer in a reproducible manner. However, total surface density of (amino)propylsilyl groups on the surface is lower than in multilayers formed under aqueous conditions. The gas-phase deposition of a single surface-saturated molecular layer can be performed by various chemical vapor deposition (CVD) techniques but especially by ALD which also enables a simple control of the surface density and the film thickness, as will be discussed in Section 2.2. ALD is not only closely related to CVD, but also to grafting.[8]

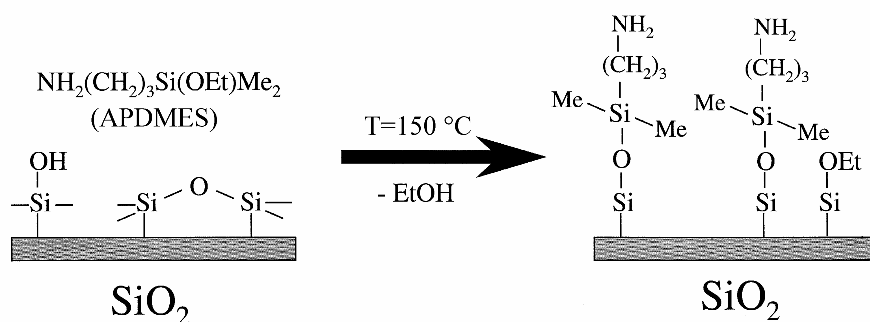



**Figure 2**. Gas-phase deposition of γ-aminopropylethoxydimethylsilane (APDMES) on silica heat-treated at 600-800 °C.[III]

Despite the advantages offered by gas-phase deposition, silylation of surfaces is mostly performed from the liquid phase.[1] Moreover, liquid-phase studies of silanes far outnumber gas-phase studies. Several studies involving the gas-phase silylation of various surfaces have nevertheless been reported in the literature; most of them are summarized in Table 1. The aim of the studies was the preparation and study of the deposition of functionalized surfaces, except for those of Tedder et al.[47] and Ferguson et al.[48] where the interest was the deposition of silicon dioxide layers on substrates using tetraethoxysilane (TEOS) as the precursor. The use of chlorosilanes has been widely studied for the silylation of surfaces but the formation of hydrochloric acid results, and may cause leaching of the molecular layer and chlorination of the original substrate.[1] One way to avoid leaching and chlorination is to use aminopropylalkoxysilanes.

**Table 1.** Studies on the gas-phase deposition of silanes on porous and planar substrates.

| **Silane** | **Substrate** | **Reference** |
|---|---|---|
| *Alkoxysilanes* | | |
| Tetraethoxysilane (TEOS)<br>without a catalyst<br>with $NH_3$ as catalyst | <br>Pyrogenic silica<br>$BaTiO_3$ and $ZrO_2$ particles | <br>47<br>48 |
| Tetramethoxysilane (TMOS) | Pyrogenic silica | 49 |
| Methyltriethoxysilane (MTES) | Silica disk | 50 |
| 1H,1H,2H,2H-Perfluorodecyltriethoxysilane | Ge/Ge oxide | 51 |
| Methyltrimethoxysilane (MTMS) | Silica disk<br>Pyrogenic silica | 50,54,55<br>49 |

| | | |
|---|---|---|
| 3-Glycidoxypropyltrimethoxysilane<br>with triethylamine (TEA) as the catalyst | <br>Silica gel | <br>6 |
| n-Octadecyltrimethoxysilane | Silicon wafer | 56 |
| Heptadecafluoro-1,1,2,2-tetrahydrodecyl-1-trimethoxysilane | Silicon wafer | 56 |
| 3-Mercaptopropyltrimethoxysilane (MPTMS) | Pyrex glass and quartz | 57 |
| Dimethyldimethoxysilane (DMDM) | Silica disk<br>Pyrogenic silica | 50,58<br>49 |
| Methyldimethoxysilane (MDMS) | Silica disk | 50 |
| Trimethylethoxysilane (TMES) | Silica disk<br>Silica gel<br>MCM-41 silica | 50<br>52<br>53 |
| Dimethylmonoethoxysilane | Silica gel | 52 |
| Trimethylmonomethoxysilane (TMMS) | Silica disk<br>Pyrogenic silica | 50,58<br>49 |
| *Aminoalkoxysilanes* | | |
| γ-Aminopropyltriethoxysilane (APTS) | Oxidized Al<br>Silicon wafer<br>Silica gel | 63<br>64<br>6,18,59-61,65, 66, III-VI |
| γ-Aminopropyltrimethoxysilane (APTMS) | Silica gel | III,V,VI, 59-61 |
| N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AAPS) | Silica gel | 59,60, 63,VII |
| n-(6-Aminohexyl)aminopropyltrimethoxysilane | Silicon wafer | 56 |
| γ-Aminopropyldiethoxymethylsilane (APDMS) | Silica gel | 59-61,III,V |
| γ-Aminopropyldimethylethoxysilane (APDMES)<br>without a catalyst<br>with TEA as catalyst | <br>Silica gel<br>Silica gel | <br>19,III,59-61,67<br>67 |
| *Chloro- and iodosilanes* | | |
| Heptadecafluorodecyltrichlorosilane (HFTS) | Glass coated with $SiO_2$ | 68,69 |
| Trifluoropropyltrichlorosilane (TFTS) | Glass coated with $SiO_2$ | 68 |
| Nonafluorohexyltrichlorosilane (NFTS) | Glass coated with $SiO_2$ | 68 |

| | | |
|---|---|---|
| 3-Bromopropyltrichlorosilane | Glass and quartz wafer | 57 |
| Trichloromethylsilane (TMCS) | Silica disk<br>Silica gel<br>MCM-41 silica and Ti-MCM-41 | 50<br>70,71<br>53 |
| Dichlorodimethylsilane | Silica gel | 72, 73 |
| 1,3-Dichloro(tetramethyldisiloxane) | Silica gel | 72 |
| 1,5-Dichloro(hexamethyltrisiloxane) | Silica gel | 72 |
| 1,7-Dichloro(octamethyltetrasiloxane) | Silica gel | 72 |
| 1-(Dimethylchlorosilyl)-2-(p, m-chloromethylphenyl)ethane (DMCSE) | Pyrex glass and quartz wafer | 68 |
| p-Tolyldimethylchlorosilane (TDMCS) | Pyrex glass and quartz wafer | 68 |
| Tris(trimethylsiloxy)chlorosilane (TMSCl) | Silicon wafer | 74 |
| Alkylchlorosilanes ($CH_3$-$(CH_2)_{n-1}$$(CH_3)_2$Si-Cl, n=4,8,18, or 30)<br>n-Alkylmethyldichlorosilanes (H$(CH_2)_n$-Si$(CH_3)$-$Cl_2$, n=1-18)<br>Alkyltrichlorosilanes (H$(CH_2)_n$-Si-$Cl_3$), n=1-18) | Quartz slides and pyrogenic silica<br>Silicon wafer<br>Silicon wafer | 24<br>75<br>75 |
| 1H,1H,2H,2H-Perfluorodecyldimethylclorosilane | Ge/Ge oxide and Ge/$SiO_2$ | 51 |
| Trimethyliodosilane | Silicon wafer | 76 |
| *Aminosilanes (without alkoxy groups)* | | |
| $CH_3$-$(CH_2)_{17}$-Si$(CH_3)_2$-N-$(CH_3)_2$ | Quartz slides and pyrogenic silica | 24 |
| Bis(dimethylamino)dimethylsilane (BDMADMS) | Quartz disk | 77 |
| 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) | Quartz disk<br>Silica gel<br>γ-Alumina | 78<br>79, 81<br>80 |
| *Other silanes* | | |
| Triethylsilanol (TES) | Silica disk | 50 |
| (Trimethylsilyl)trifluoromethanesulfonate | Silicon wafer | 76 |

## 2.2 Atomic layer deposition

### 2.2.1 Principle of ALD

Atomic layer deposition technique based on sequential surface-saturated gas-phase reactions for surface coating and molecular engineering was developed in Finland over thirty years ago.[25-26] Initially, it was called atomic layer epitaxy (ALE), where the Greek word epitaxy means "on-arrangement". In reality, epitaxial growth can only be achieved by depositing a single crystalline layer on a single crystal. ALE is mostly used, however, for the deposition of amorphous or polycrystalline thin films on the surface of a nonmatching substrate. In general, also the steric hindrances induced by the size of the precursor molecules forbid epitaxial growth. Especially when this technique is applied for the deposition of precursor molecules onto amorphous and porous supports, atomic layer epitaxy is not the best choice of name. For this reason, the more general term atomic layer deposition (ALD) is used in the present study. In fact, several other names in addition to ALE and ALD, are found in the literature, e.g. atomic layer chemical vapor deposition (ALCVD), atomic layer growth (ALG), digital layer epitaxy (DLE), and molecular layer epitaxy (MLE) or molecular layer deposition (MLD).[30,82] The terms MLE and MLD are used to widen the scope of the ALE/ALD concept for a new class of materials containing organic and organic/inorganic multilayers. There are also modified versions of ALD, e.g. molecular designed dispersion (MDD),[83-85] where the precursor is vaporized and reacted with the surface in the same chamber. ALD can be classified as a special mode of CVD.[8]

The surface-controlled growth mechanism of ALD is based on separate gas-solid reactions of precursor molecules with the solid surface until surface saturation.[27-35] Before deposition the porous surface has to be stabilized by heat-treatment to ensure surface-controlled growth. The precursors are alternately led onto the substrate, with an inert gas purge after each reaction. Purging removes physisorbed precursor molecules and volatile reaction products from the surface. The principle of ALD with tetraethoxysilane and water as precursors is shown in Figure 3. The reaction of TEOS with the silanols of the silicon dioxide surface results in a direct formation of chemical bonds between the reactant and the substrate. At the same time, ethanol molecules are released. The following water feed results in the hydrolysis of free ethoxy groups and the release of ethanol. Thus, a surface covered with silanols is formed. These TEOS/water cycles can be repeated, and the film thickness can be controlled through

the number of cycles applied. Adjacent OH groups, shown in Figure 3e, further form siloxane bridges due to the crosslinking (i.e. condensation) reactions, which eventually result in the formation of silicon dioxide. The procedure shown can be accomplished at room temperature with use of ammonia as catalyst.[48]

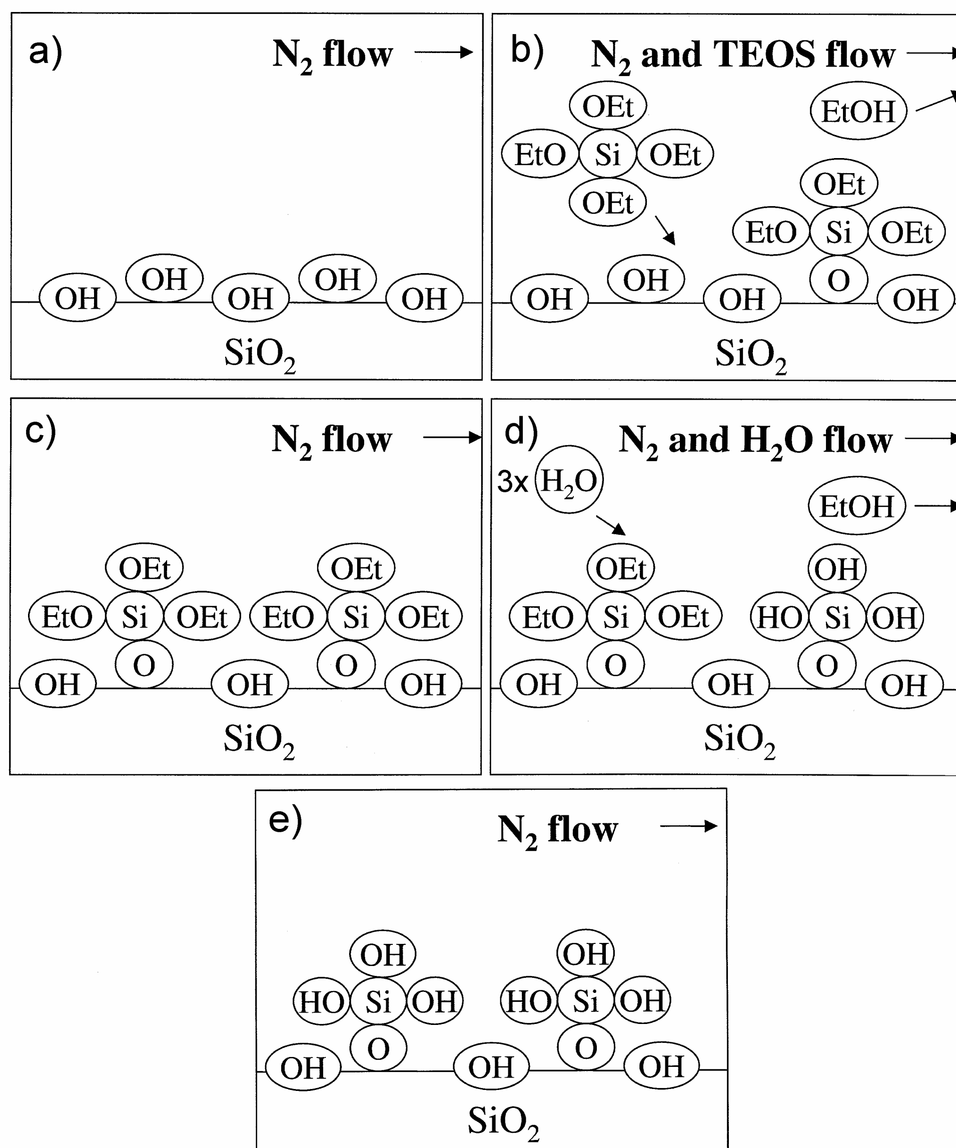



**Figure 3.** Principle of ALD: (a) Silicon dioxide surface covered with hydroxyl groups, (b) first precursor feed (TEOS), (c) inert gas purge ($N_2$), (d) second precursor feed (water), and (e) inert gas purge. Nitrogen is used as both purging and carrier gas.

Surface-limiting ALD growth is independent of the flow parameters and number of precursor molecules. However, to achieve surface saturation, the number of precursor molecules has to be at least equal to the number of reactive sites on the surface. The optimal temperature range for ALD growth occurs in the so-called ALD window, where the growth rate nearly stays

constant (Figure 4). In the case of insufficient precursor reactivity and desorption, the growth rate is distinctly less than one monolayer per cycle while in the case of reactant condensation or decomposition the growth rate is greater than one monolayer per cycle. In practice, the growth rate is less than one monolayer per cycle. The expression “growth rate” is generally used when ALD is employed on planar substrates, whereas in the case of porous surfaces the expression “surface density of adsorbed species” may be more appropriate. The factors affecting the surface density are the reaction temperature, the reactive species on the substrate, the steric hindrance, and the surface chemistry between the precursor and the support (bonding mode).[22] Theoretical studies on the factors affecting the surface density of precursors were recently carried out by Puurunen.[41]

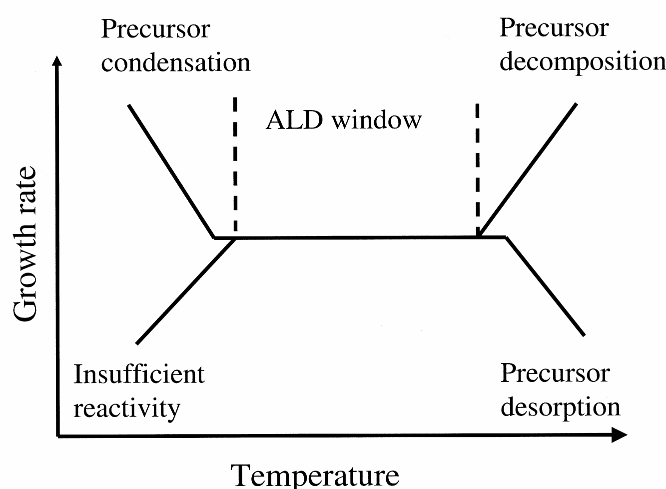



**Figure 4.** The dependence of temperature on the growth rate and the ALD window after Suntola [26].

### 2.2.2 Applications of ALD

Atomic layer deposition has been applied for the deposition of thin films onto planar substrates. One commercial application of ALD is the manufacture of thin film electroluminescent (TFEL) flat panel displays where the various layers in the insulator-semiconductor-insulator structure are grown by ALD.[26,30] ALD is being widely studied both in research institutes and in industry, and it is likely to find new applications in microelectronics in the near future. In fact, the semiconductor roadmap has recently

announced ALD to be the method-of-choice for the deposition of highly insulating high-k oxide layers onto silicon.[85,86]

The adsorption controlled growth on planar (or curved) and porous substrates represents two extreme cases in terms of surface area and number of molecular layers (reaction cycles) processed.[22] Typically, numerous reaction cycles are employed for the deposition of thin films on planar substrates by ALD, the exact number depending on the desired film thickness. In addition to the deposition of thin films on planar substrates, ALD has successfully been used for the deposition of a single or several surface-saturated molecular layers onto high-surface-area substrates. Just as on planar substrates, conformal ALD growth can be achieved on porous substrates.[88]

The first studies involving atomic layer deposition onto porous substrates were carried out over a decade ago with the aim of preparing heterogeneous catalysts. Sequential surface reactions of metal precursors and oxidizing agents were applied for the preparation of multilayered metal oxide,[89-91] nitride,[92] and silicate[93] structures. Almost all studies reported in the literature based on the modification of porous surfaces by ALD are focused on catalytic applications.[38-43,94] Most of the literature concerning the use of ALD for the preparation of catalysts has recently been reviewed.[41] It has been concluded that catalysts with improved and controlled dispersion can be prepared by ALD. For instance, the rate of propene formation is observed to be doubled relative to impregnated vanadium pentoxide catalysts when catalysts prepared by ALD are applied to the dehydrogenation of propane to propene.[40,95] The acid-base characteristics of $V_2O_5$ catalysts are also strongly affected by the preparative route.[40,96] As Burtman et al.[3,4] have shown, ALD enables easy processing of multistructured organic components, e.g. polyimides, on the surface. Further, new properties and applications for the materials may be found with better surface tailoring. Recently, ALD has been used for the deposition of thin films on porous silicon for sensor applications.[97]

Regardless of the type of substrate used, for a reproducible result one needs good knowledge of the chemical reactions taking place in each reaction sequence.[22] ALD growth on a porous surface can be conveniently followed step-wise after each reaction sequence, i.e. deposition of a single surface-saturated molecular layer of certain precursor molecules on the surface. The growth mechanisms can then be understood on the molecular level, and valuable information on the gas-solid reactions can be obtained. Because of the large specific surface area of the

porous substrate, a large surface covered with reactive surface species is available for the modification and analysis. Elemental analyses, solid-state NMR, and DRIFTS can be used to characterize powder samples. The use of these characterization techniques enables study of the type of surface reaction (e.g. ligand exchange or addition reaction) and the bonding mode of precursor molecules on the surface. Further, the information obtained for porous substrates can be applied to thin film depositions because the surface chemistry is the same on planar and porous surfaces of the same substrate material.

### 2.2.3 Requirements for substrate, precursor, and reaction conditions

Under properly selected saturation conditions, ALD growth is highly reproducible and the resulting samples are homogeneous. In order to achieve ALD growth, however, the substrate, precursor and reaction conditions have to fulfill certain basic requirements.[22] When these preconditions are met the surface coverage is homogeneous throughout the sample and ALD growth is reproducible from sample to sample.

*Substrate.* The physical properties, including the specific surface area, pore volume, and average pore diameter, have to be taken into account in selecting a porous substrate. If there are enough bonding sites on the surface, a high surface area enables the adsorption of a large number of precursor molecules on the substrate, while a large pore diameter also enables the large precursor molecules to penetrate into the pores. Knowledge of the surface species on the substrate is important because of the surface-controlled nature of the growth in ALD.[98] The characterization of surface is of particular importance in the case of porous substrates when only one or a few reaction sequences are usually applied. The substrates most frequently used are oxides. For instance, porous silica is typically terminated with various types of OH groups and oxygen bridges, which serve as the reactive sites.[1] Porous substrates are always stabilized by heat treatment before deposition when physically bound water molecules are removed and the number and nature of the surface species can be controlled.

*Precursor.* The main requirements for the precursor molecules are sufficiently high vapor pressure and thermal stability at the processing temperature. By reducing pressure in the reactor lower vaporization temperatures can be attained. The size of the precursor molecule will strongly affect the surface density achieved on the substrate.[38,41,99,100] An excess of

precursor molecules compared to the number of reactive sites on the substrate is loaded to the reactor to ensure surface saturation.

*Reaction conditions.* Various deposition temperatures may have to be explored for activation of the desired chemical reactions and for the selection of an appropriate reaction temperature. The deposition temperature may not exceed the pretreatment temperature of the substrate in order to ensure adsorption-controlled growth. The deposition temperature is practically equal to or higher than the vaporization temperature. Particularly, in the ALD process on porous materials, decomposition of the precursor, which may lead to an uneven distribution of precursor molecules or to the blocking of pores, must be prevented.

## 3. EXPERIMENTAL

The main features of the materials and ALD procedures used in the experiments are presented in this section. The methods used to characterize the surface species on both the plain substrate and deposited atomic layers are briefly introduced. The experimental details can be found in the original publications I-VII.

### 3.1 Materials

Nine amorphous silicon dioxide samples of various types were used to test the characterization methods applied in this study.[I,II] The silica samples for the DRIFTS and $^1H$ MAS NMR measurements were pretreated in a muffle furnace in air at 105, 550, or 1000 °C for 16 h. The most important physical properties of silica, i.e. specific surface area, pore volume, and average pore diameter, were determined by nitrogen physisorption and laser diffraction measurements.

EP $10_x$ silica gel from Crosfield, UK, in the atomic layer depositions were used as the support. The specific surface area (Brunauer-Emmett-Teller, BET), the pore volume, and the average pore diameter of EP $10_x$ as determined by a standard nitrogen physisorption technique were 300 $m^2 g^{-1}$, 1.2 $cm^3 g^{-1}$, and 20 nm, respectively. The specific surface area of EP $10_x$ heat-treated at 800 °C was diminished to 280 $m^2/g$ and the pore volume to 1.0 $cm^3/g$. The average particle size of EP $10_x$ was 100 µm, as reported by the manufacturer. Silica for the deposition experiments was stabilized by pretreatment at 200, 450, 600, and 800 °C in the manner described above. The numbers of silanol groups were determined by $^1H$ MAS NMR.

Commercial trifunctional γ-aminopropyltrimethoxysilane (APTMS), γ-aminopropyl-triethoxysilane (APTS), and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPS); bifunctional γ-aminopropyldiethoxymethylsilane (APDMS); and monofunctional γ-amino-propyldimethylethoxysilane (APDMES) were used as precursors for the modification of silica. AAPS, APDMS, and APDMES were obtained from ABCR, Germany; APTMS from ABCR, Germany, and Aldrich, U.S.A.; and APTS from Merck, Germany. The source materials in the preparation of imide structures on aminosilylated silica were pyromellitic anhydride (PMDA) and 1,6-diaminohexane (DAH) obtained from Fluka Chemika, Germany. The purity of the reagents was >95%. The schematic structures of the precursors are shown in

Figure 5. Distilled water was used for the hydrolysis and deuterated water for the deuteration of the alkoxy groups of aminosilylated silica samples.

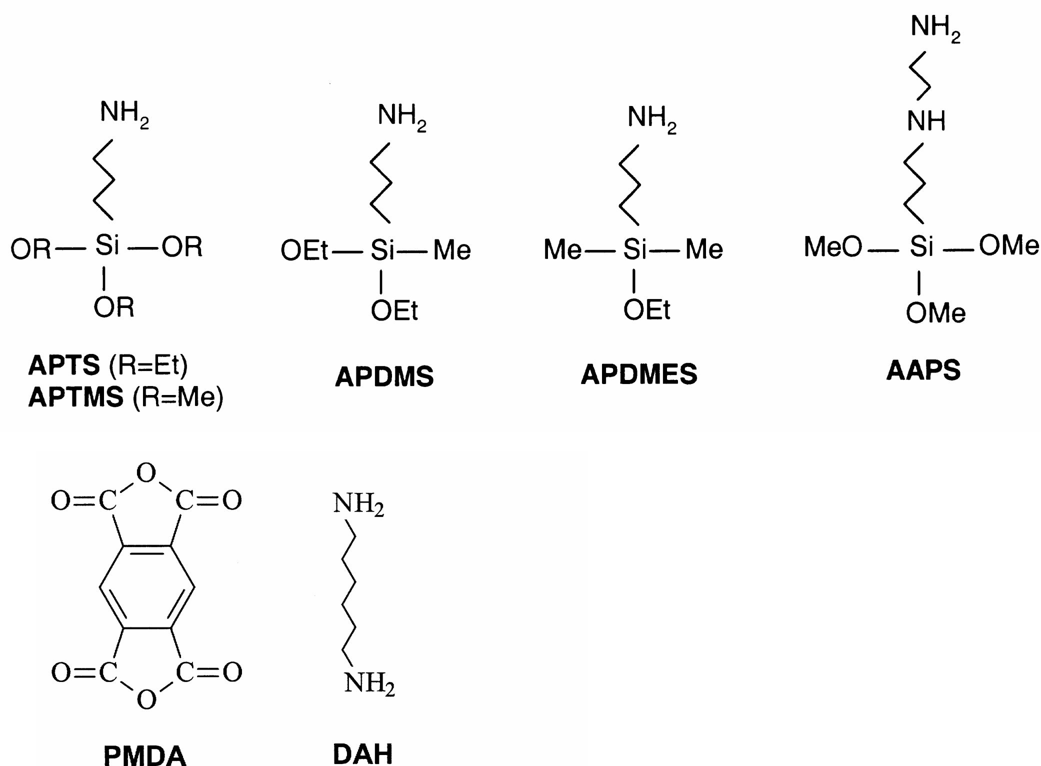



**Figure 5.** Schematic structures of the precursors.

## 3.2 ALD procedure

### 3.2.1 Deposition of a single surface-saturated molecular layer of γ-aminopropylalkoxysilanes and a high-density aminopropylsiloxane network

Precursors were introduced onto silica via the gas phase by ALD. The ALD reactor (F-120, ASM Microchemistry Oy, Helsinki, Finland) used for the depositions is shown in Figure 6. First heat-treated silica (4-5 g) was pretreated in the ALD reactor at 150-180 °C under pressure of 2-5 kPa in flowing nitrogen for 120-180 minutes in order to remove the physisorbed water from the surface. The precursors were placed in crucibles and vaporized at 90-130 °C. The pulse lengths were 180 or 210 minutes. The deposition process was studied at reaction temperatures ranging from 125 to 300 °C. In all experiments, the deposition temperature was lower than the pretreatment temperature of silica. Physisorbed precursor molecules were purged from the surface with nitrogen gas (>99.999 %), after which only the

chemisorbed precursor molecules remained on the surface. No further heat-treatment after the deposition process was performed. Modified samples were taken from the surface and bottom of the silica bed under ambient conditions and were stored in a desiccator to avoid hydrolysis of the alkoxy groups due to air humidity.

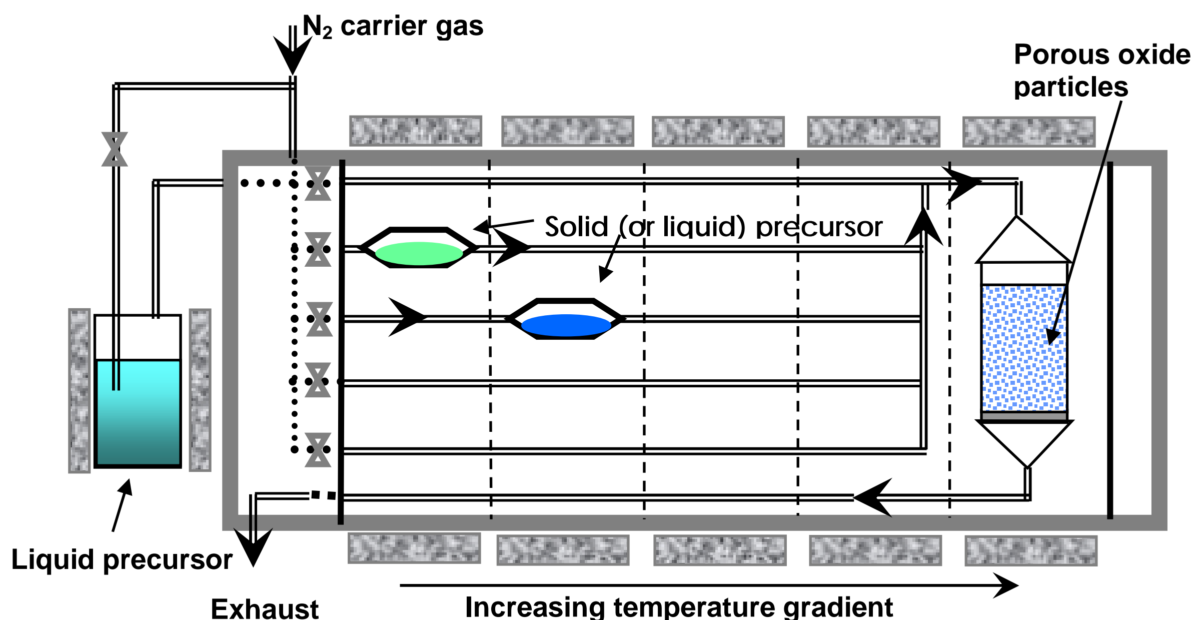



**Figure 6.** Flow-type ALD reactor used for deposition after Haukka[38].

Sequential reactions of trifunctional γ-aminopropylalkoxysilanes and water for the deposition of a high-density aminopropylsiloxane network on silica were applied. The pretreatment temperature of silica (10 g) was 450 °C and the reaction temperature was 150 °C. During the first reaction sequence, silica was treated with the silane precursor and during the second reaction sequence aminosilylated silica was treated with water vapor to hydrolyze the free alkoxy groups. These two sequences, referred to here as one cycle, were repeated from one to five times (six times for AAPS). Both the aminosilane precursor and water were vaporized in crucibles one at a time. For the removal of unreacted reactants, each reaction sequence was followed by a nitrogen purge at the reaction temperature. For APTMS, the first hydrolysis sequence was performed with deuterium oxide at 150 °C in order to detect unreacted silanol groups on silica pretreated at 600 °C by DRIFTS.

### 3.2.2 Deposition of several surface-saturated molecular layers of organic precursors

The deposition process was performed essentially as outlined above. Aminosilylated silica was allowed to react at 200-220 °C with PMDA which was vaporized at 190-215 °C. Next DAH, vaporized at 80 °C, was reacted with the PMDA -modified surface at 200 °C.

## 3.3 Characterization techniques

Various analytical methods were used for characterization of physical and chemical properties of silica. Nitrogen physisorption (BET) and laser diffraction were used for characterization of the physical properties of silica, while the other methods shown in Table 2 were used for the qualitative and quantitative characterization of the surface species on silica. PLS, a multivariate calibration of the DRIFT spectra, for the quantitative study of the hydroxyl groups in heat-treated silica, was used.[II] TG was used as a reference method for the determination of the OH concentrations.[I] In turn, the results obtained from the TG measurements were compared with $^{1}H$ MAS NMR results. The aminosilylated silica samples (Table 2) were characterized by DRIFTS and $^{1}H$ MAS NMR, in the same way as the silica samples. $^{13}C$ and $^{29}Si$ CP/MAS NMR were applied for qualitative characterization of the aminosilylated silica samples and elemental analyses for quantitative analysis.

**Table 2.** Analytical techniques used for the characterization of silica and aminosilylated silica.

| Technique | Information | Publication |
|---|---|---|
| Nitrogen physisorption (BET) | Specific surface area, pore volume and average pore diameter of silica | I-VII |
| Laser diffraction | Average particle size of silica | I |
| Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) | Qualitative and semiquantitative determination of surface species on silica and aminosilylated silica | II, III, VI, VII |
| Solid-state nuclear magnetic resonance spectroscopy (NMR) | Qualitative and semi/quantitative determination of surface species on silica and aminosilylated silica | I, III-VII ($^{1}$H MAS NMR) IV, V ($^{29}$Si CP/MAS NMR) V-VII ($^{13}$C CP/MAS NMR) |
| Projections to Latent Structures by means of partial least squares (PLS) | Quantitative determination of surface species on silica together with DRIFTS | II |
| Thermogravimetry (TG) | Quantitative determination of surface species on silica | I, II |
| Elemental analyses | Quantitative determination of the number of nitrogen and carbon atoms on aminosilylated silica | III-VII |

# 4. RESULTS AND DISCUSSION

The effect of heat treatment on the various surface species of porous silica was studied by DRIFTS, and the effect on the silanol groups of silica by TG, $^{1}H$ MAS NMR, and DRIFTS/PLS. ALD was applied for the modification of silica by depositing a single surface-saturated layer of γ-aminopropylalkoxysilanes on the silica surface. Especially, the effects of pretreatment temperature of silica, type of precursor, and the reaction temperature were of interest. The use of ALD for the deposition of a high-density aminopropylsiloxane network was studied, and finally, the growth of polyimide structures on aminosilylated silica was investigated. The results of the studies are reported below.

## 4.1 Characterization of silica

One of the goals of this work was to adapt existing physical techniques, such as TG and DRIFTS, for a quick and simple characterization of the surface species on silica. Although chemical methods based on the use of a selective and well-known chemical reaction of a monofunctional probe molecule[1], e.g. hexamethyldisilazane, with the surface species could have been used for characterization, they were not studied in this work. The advantage of chemical methods is that internal silanols, not of particular interest in adsorption studies, can be excluded from the detection procedure. In physical methods they are usually included.

### 4.1.1 Qualitative study of the effect of heat treatment on the surface species of silica by DRIFTS

The relative numbers of surface species on silica (Figure 7) are altered through heat treatment.[1, 101-103] At the beginning of heat treatment, at 100-200 °C, physically adsorbed water molecules desorb from the porous silica surface in a process called dehydration.[102,104-107] After dehydration the silica surface is covered with vicinal, i.e. strongly hydrogen-bonded, and isolated silanols. Hydrogen bonds between two silanols are formed when the distance between them is less than 0.33 nm and the surface geometry is suitable; otherwise the silanols are isolated.

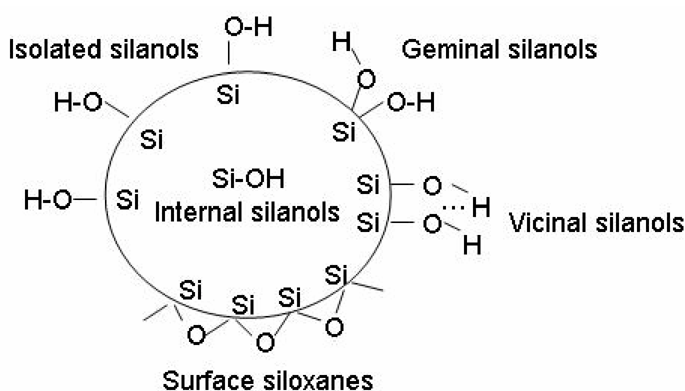
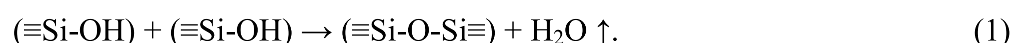



**Figure 7.** Surface species on and inside a silica particle after Zhuravlev[102].

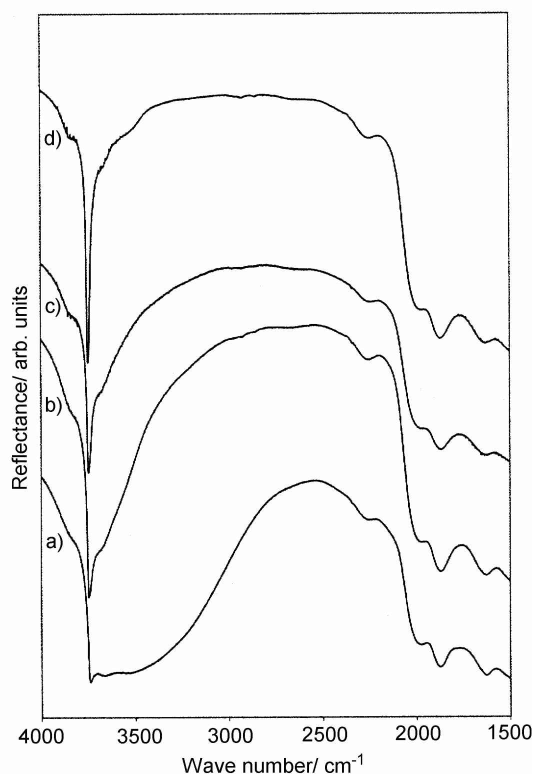
As the heat treatment is continued, the silanol groups begin to desorb and dehydroxylation occurs. First, the vicinal hydroxyls react and form isolated silanols and siloxane bridges on the surface. Most of these types of silanols react within a quite narrow temperature region of 200-400 °C.[1,104] However, the dehydroxylation reaction of vicinal silanols may begin already at 110 °C and continue up to 600°C.[1]

The decrease in the number of strongly and weakly hydrogen-bonded hydroxyl groups on the silica surface during heat treatment was clearly observed in the region 3700-3500 $cm^{-1}$ in the DRIFT spectra of heat-treated silica samples (Figure 8). The intensity of bands for strongly hydrogen-bonded and weakly H-bonded (internal) OH groups distinctly decreases when the pretreatment temperature is raised from 200 to 600 °C.[1,38,94,108] Isolated silanols are seen as a sharp and strong peak at 3748-3740 $cm^{-1}$ in the DRIFT spectra of all silica samples regardless of pretreatment temperature. In IR spectroscopy, the isolated and geminal silanols are called free silanols and the hydrogen-bonded silanols bridged or perturbated silanols.[1] When the silica is heated up to higher temperatures, isolated silanols slowly start to react and the water molecules desorb from the surface. Vicinal and isolated silanols partly react in the same temperature region. At temperatures higher than 600 °C the silica surface is mainly covered with isolated silanols. Isolated silanols react with one other to form stable siloxane bridges:



$$(\equiv Si\text{-}OH) + (\equiv Si\text{-}OH) \rightarrow (\equiv Si\text{-}O\text{-}Si\equiv) + H_2O \uparrow. \quad (1)$$

The nature of the heat-treatment (isothermal or dynamic) and the ambient pressure strongly affect the dehydroxylation reaction. Also the size and number of pores on the silica affect the desorption of water from the surface.




| Wave number/ $cm^{-1}$ | Assignment |
|---|---|
| 3748-3740 | free (isolated and geminal) Si-OH |
| 3680-3650 | bridged and internal (weakly hydrogen-bonded) Si-OH |
| 3550-3500 | bridged and vicinal (strongly hydrogen-bonded) Si-OH |

**Figure 8.** DRIFT spectra of silica heat-treated at (a) 200, (b) 450, (c) 600, and (d) 800 °C.[III]

### 4.1.2 Determination of surface silanol groups by TG and $^{1}$H MAS NMR

Thermogravimetry can be used for quantitative determination of the silanol groups on silica,[1,105,109-113,I] with the limitation that distinguishing of the hydrogen-bonded and isolated silanols on the basis of thermograms (Figure 9) is not possible due to the partly occurring simultaneous dehydroxylation reactions. The condensation of all types of silanol groups occurs by the reaction of two adjacent silanol groups on the silica surface resulting in the release of one molecule of water and the formation of one siloxane group. The hydroxide group content, determined as moles of hydroxyls left per gram of silica at temperature $T_0$, can be calculated as follows:

$$n_{OH}\,(mol/g\ SiO_2) = 2 \cdot n_{H2O} = 2(WL(T_0)-WL(T_{final}))/(100 \cdot M_{H2O}), \qquad (2)$$

where $WL(T_0)-WL(T_{final})$ is the second weight loss in the temperature region $T_0$-$T_{final}$ and $M_{H2O}$ is the molar mass of water.

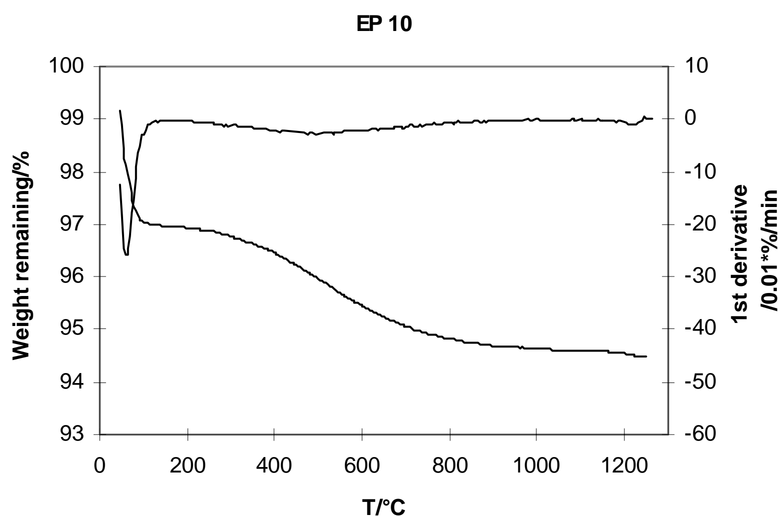



**Figure 9.** Thermogram of EP 10 silica (20 mg) heated at a rate of 5 °C $min^{-1}$ under argon flow.[I]

In this work, the OH group contents determined by dynamic TG measurements from several silica samples[I] were in good agreement with the results obtained by a reference method, $^1H$ MAS NMR[38] (magic angle spinning NMR). The samples for NMR analysis were heat-treated under a static air atmosphere in a muffle furnace. Not only the total hydroxyl group contents (determined by TG at 100-130 °C) but also the hydroxyl group contents determined by TG at 550 (Figure 10) and 1000 °C were very close to the $^1H$ MAS NMR results.[I] There was a larger difference between the methods, however, in regard to the number of OH groups in silica samples determined at 1000 °C. The results for EP 10 silica are shown in Table 3.

The TG method described above can easily be applied, especially for the determination of the total OH group content and the silanol number, but unfortunately not so reliably for the determination of OH groups at temperatures higher than 550 °C. The greatest differences between the results of the two methods were observed with the powder-like silicas MCM-41 and Aerosil pressed into briquettes before the TG measurements (Figure 10). In earlier studies, the OH group contents calculated from the TG results were not compared with the results from a reference method. [1,105,109-113]

**Table 3.** Results from TG and $^{1}$H MAS NMR measurements of EP 10 silica.

| | TG | | | | NMR | |
|---|---|---|---|---|---|---|
| **Temp./ °C** | **Mass loss/ %** | **OH group content/ mmol/g** | **OH group content/ mg/g** | **Silanol number/ OH/nm$^2$** | **OH group content/ mg/g** | **Silanol number/ OH/nm$^2$** |
| 115 | 2.6 | 2.9 | 48 | 5.4 | 54 | 6.0 |
| 550 | 1.2 | 1.3 | 23 | 2.4 | 20 | 2.2 |
| 1000 | 0.11 | 0.12 | 2.0 | 0.9 | 2.4 | 1.1 |

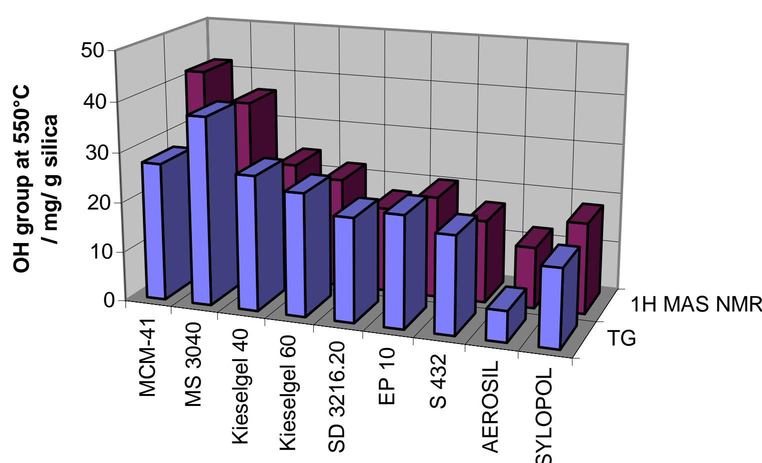



**Figure 10.** Comparison of the OH group contents measured by TG and $^{1}$H MAS NMR in various silica samples heat-treated at 550 °C.[I]

Modern NMR techniques, especially solid-state magic angle spinning, give valuable information on the structure and dynamics of surfaces.[1] $^{29}$Si CP/MAS NMR can be employed for the determination of the total number of OH groups in silica and to distinguish the geminal silanols from the isolated and vicinal silanols. In $^{29}$Si NMR studies, geminal silanols are called double silanols or silanediols and both isolated and vicinal silanols single silanols.[1] $^{1}$H MAS NMR complements $^{29}$Si NMR since it enables separate determination of the isolated and H-bonded silanols, both qualitatively and quantitatively. In the present work, the CRAMPS (combined rotation and multiple pulse spectroscopy) technique developed by Bronnimann et al.[114] was applied for the determinations.[115,116] A reference sample with a known number of hydroxyl groups was used for the quantification of the silanol groups. The total number of OH groups is determined from the surface area of peaks in the NMR spectrum

and the relative numbers of isolated and H-bonded silanols from the deconvolution algorithms. The concentrations of the silanols on silica pretreated at 200, 450, 600 and 800 °C are shown in Figure 11. As determined by Kiselev and Zhuravlev,[102] the silanol number for the completely hydroxylated surface mostly varies between 4.2 and 5.7 OH $nm^{-2}$ regardless of the type of silica.

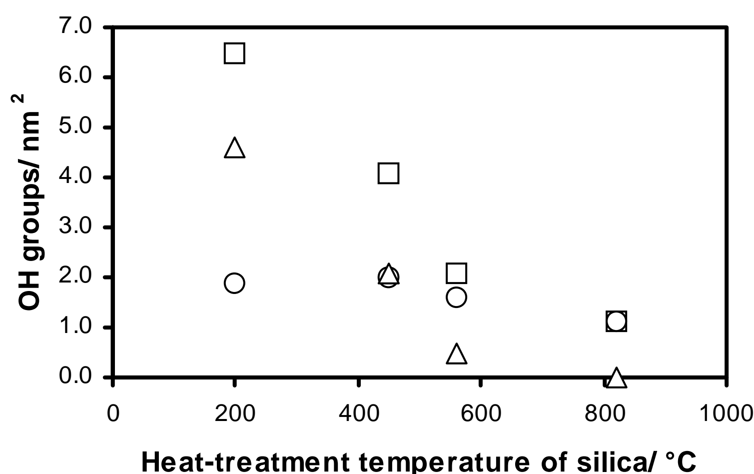



**Figure 11.** Silanol groups on EP 10 silica determined by $^{1}H$ MAS NMR: ○ isolated silanols, Δ hydrogen-bonded silanols, □ total number of silanols.[I,III]

### 4.1.3 Quantitative determination of silanol groups by DRIFTS/PLS procedure

Qualitative determination of the surface species on an unmodified or a chemically modified silica sample is generally performed directly from the undiluted sample by FTIR. In this case, the reflectance of the specular component is included in the reflectance values, which leads to artifacts, i.e. scattering and baseline shifts, in the DRIFT spectra. In addition to the concentration, particle size distribution, sample preparation, and height of sample holder affect the intensities and surface areas of the peaks.[117,118] Because of this, sample dilution with KBr or a comparable substance is preferred, especially in quantitative studies. According to the Kubelka-Munk theory, the spectral intensities are linearly dependent to the analyte concentrations when the samples are dilute and uniformly ground. Quantitative analysis always requires calibration, which can be performed, for example, by normalizing the surface areas of the peaks studied to a reference band, whose intensity remains unchanged.[1]

Various signal-processing techniques, e.g. orthogonal signal correction (OSC), have been developed to overcome the above-mentioned sources of artifacts.[118] In the present study[II], a method based on multivariate calibration, projections to latent structures by means of partial least squares (PLS), was used. The data pretreatment was performed with OSC prior to the PLS modeling. The principle of multivariate calibration in FTIR is such that every wave number is treated as a variable. Chemometrics is generally used to solve problems where there is a lot of multivariate data with correlations. [119-123] Multivariate techniques, like PLS, have been found to be especially useful in process analysis.

The entire DRIFT spectrum for each sample was used for the creation of the model. The data more closely matched the predicted trend when the entire wave number region was used, than when only a single wave number was used. Thermogravimetry (TG) was used as a reference method to quantitatively determine the total number of hydroxyl groups on silica samples. The calibration model was validated by predicting the hydroxyl content of samples not used in the construction of the models. The OSC-PLS model was able, with sufficient accuracy, to predict the hydroxyl content of silica samples with different physical properties heat-treated at various temperatures (Figure 12). The root mean squared error of prediction (RMSEP) was 0.00707 g(OH)/g(silica).[II]

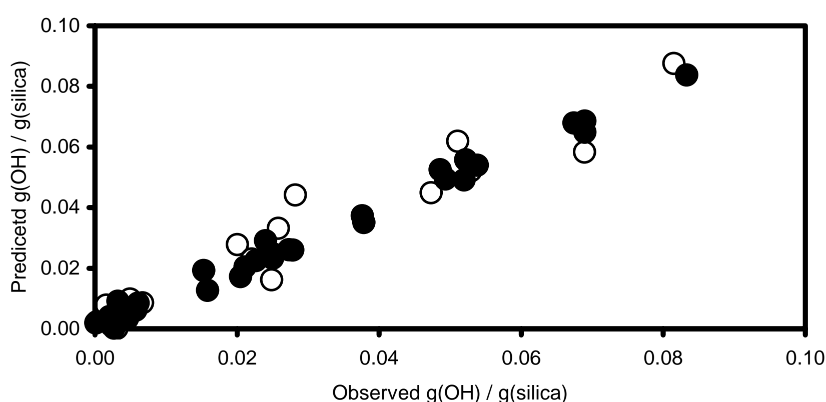



**Figure 12.** Observed versus predicted concentrations of OH groups for the OSC-PLS model. ● refers to the calibration set and ○ to the test set.[II]

The advantage of the present method is that, after creation of the model, the total numbers of hydroxyl groups of numerous samples can be determined very quickly. Only the DRIFT spectrum of an unknown heat-treated silica sample has to measured. However, the model can be utilized only for the same type of silica samples used in creation of the model.

### 4.2 Modification of silica with γ-aminopropylalkoxysilanes

Studies were made of the effects of pretreatment temperature of silica, type of precursor, and the reaction temperature on the deposition of γ-aminopropylalkoxysilanes on silica. The use of ALD for the deposition of a high-density aminopropylsiloxane network on silica was also studied.

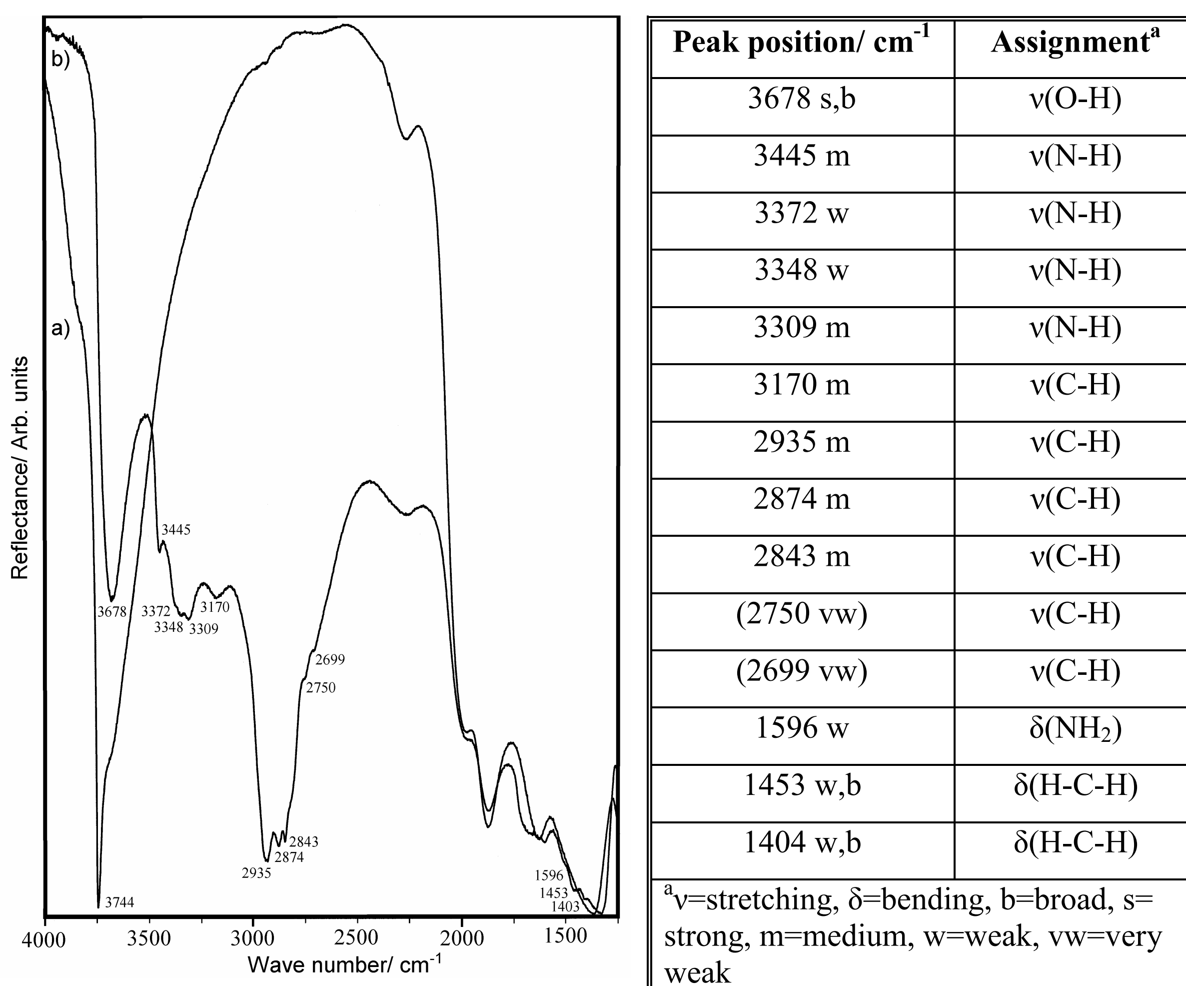
#### 4.2.1 Deposition of a single surface-saturated molecular layer of γ-aminopropylalkoxysilanes on silica

According to both DRIFT spectra and elemental analyses, the modified silica bed was evenly covered by the chemisorbed precursor molecules at 150 °C.[III-VII] Thus, the reaction of vaporized aminosilanes with the silica surface pretreated at 200-800 °C was surface-limited at the reaction temperature of 150 °C. The effect of higher reaction temperatures on the surface species that formed will be discussed in Section 4.2.1.2. Here, the modification of silica will be discussed only for silica heat-treated at 450 °C, except in the deuteration experiments for silica heat-treated at 450 and 600 °C.

According to the DRIFT spectra (Figure 13), the strong O-H stretching vibration band of free silanols at 3744 $cm^{-1}$ disappears upon the reaction of silica with aminosilanes.[III,VI,VII] Both Iiskola's study[52] and the present study[III,VI] have shown that even though all isolated silanol groups on silica seem to have reacted unreacted silanol groups still exist under the aminosilane groups bonded to silica because of steric hindrance or the presence of strong hydrogen bonding. Their existence can be confirmed by a treatment with deuterated water in which way all surface hydrogen atoms are exchanged with deuterium at the same time as alkoxy groups are hydrolyzed and deuterated.[124] The OD groups that form on the surface are observed in the DRIFT spectrum as a small peak at 2760 $cm^{-1}$. At the same time, a peak corresponding to free OH groups of modified silica pretreated at 600 °C, which can be assigned to undeuterated silanol groups of silica under the alkoxy groups, appears in the spectrum. These unreacted OH groups can now be observed by IR because the large alkoxy groups covering them have vanished due to hydrolysis. These OH groups are no longer perturbated by hydrogen-bonding interactions because of large distance between them and the other OH groups or alkoxy groups. However, at low pretreatment temperature of silica, viz. at

450 °C, the sharp peak due to free silanols cannot be seen, which indicates perturbation of unreacted silanol groups because of hydrogen bonding.

After the modification of silica with aminopropylalkoxysilanes, a strong and broad band next to free silanols is seen in the DRIFT spectra at 3680-3640 $cm^{-1}$. In the spectra of unmodified silicas, this band appears in the same wave number region that has been assigned to internal hydroxyls inside the silica particles, which are inaccessible to most precursor molecules.[1] The broad band is likely to be due both to internal silanols and to unreacted silanols perturbated by hydrogen bonds with oxygen atoms of the alkoxy groups of aminosilanes.[87] The assignments[125] of the IR vibrations in the DRIFT spectra are shown in Figure 13 for AAPS. The reaction of precursor molecules with the silica surface can also be seen as the appearance of N-H and C-H stretching vibrations (Figure 13).




| Peak position/ $cm^{-1}$ | Assignment[a] |
|---|---|
| 3678 s,b | ν(O-H) |
| 3445 m | ν(N-H) |
| 3372 w | ν(N-H) |
| 3348 w | ν(N-H) |
| 3309 m | ν(N-H) |
| 3170 m | ν(C-H) |
| 2935 m | ν(C-H) |
| 2874 m | ν(C-H) |
| 2843 m | ν(C-H) |
| (2750 vw) | ν(C-H) |
| (2699 vw) | ν(C-H) |
| 1596 w | δ($NH_2$) |
| 1453 w,b | δ(H-C-H) |
| 1404 w,b | δ(H-C-H) |
| [a]ν=stretching, δ=bending, b=broad, s= strong, m=medium, w=weak, vw=very weak | |

**Figure 13.** DRIFT spectra of (a) silica pretreated at 450 °C and (b) a single surface-saturated layer of AAPS on silica.[VII]

#### 4.2.1.1 Effect of heat-treatment of silica and type of precursor

Surface densities were studied for five aminopropylalkoxysilane precursors deposited at 150 °C on silica surfaces pretreated at 200-800 °C. The pretreatment temperature of silica had a clear effect on the surface density of terminal amino groups as well as on the surface density of aminosilane molecules (Table 4, Figure 14). The surface densities decreased when the pretreatment temperature of silica was increased so that the densest amino-functionalized surfaces were achieved on silica heat-treated at 200 °C. The surface densities could be controlled in the range 1.0-2.1 molecules per $nm^2$ through the heat-treatment of silica and choice of the precursor.

**Table 4.** Effect of heat-treatment temperature of silica on the number of gas-phase-deposited aminopropylalkoxysilane molecules (±0.1 molec./$nm^2$) on silica.

| Heat treatment of silica/ °C | Isolated OH groups on silica/ $nm^2$ | APTS molecules/ $nm^2$ | APTMS molecules/ $nm^2$ | APDMS molecules/ $nm^2$ | APDMES molecules/ $nm^2$ | AAPS molecules / $nm^2$ |
|---|---|---|---|---|---|---|
| 200 | 1.9 | 2.0 | 1.8 | 2.1 | 1.8 | 1.7 |
| 450 | 2.0 | 1.8 | 1.6 | 2.0 | 1.8 | 1.5 |
| 600 | 1.6[a] | 1.6 | 1.3 | 1.6 | 1.5 | 1.3 |
| 800 | 1.1[b] | 1.3 | 1.1 | 1.4 | 1.3 | 1.0 |

[a] measured on silica pretreated at 560 °C; [b] measured on silica pretreated at 820 °C.

As in the case of liquid-phase depositions, the total silanol group content on silica does not affect the surface density of aminopropylalkoxysilanes deposited in the gas phase at low calcination temperatures, viz. 200-450 °C. Vrancken *et al.*[126,127] obtained results showing an equal coverage of about 2.0-2.1 molecules/$nm^2$ for APTS deposited from dried organic solvent on silica heat-treated at 200-600 °C. In the present study, at high pretreatment temperatures of silica (450-800 °C), the surface density of all precursors decreased to 1.0-1.4 molecules/$nm^2$ varying with the precursor. Just the opposite has been found in liquid-phase studies, where the surface density of APTS on silica pretreated above 600 °C was found to increase radically to about 2.8 molecules/$nm^2$.[126,127] In the present study, the numbers of amino groups obtained with single-amino group precursors and the numbers of isolated OH groups on silica (heat-treated at 200-600 °C) were almost equal. But it cannot be concluded that these precursors selectively react with isolated silanols because the molecules are not

only monodentately bound, but also bi-, and tridentately bound[V] with the silica surface. With the larger precursor molecule AAPS containing two amino groups, the number of precursor molecules on the surface was lower than the number of isolated silanols.

Exceptionally, there are more amino groups than isolated silanol groups on silica heat-treated at 800 °C when APTS, APDMS, and APDMES are the precursors. This is probably due to side-reactions occurring with reactive, strained siloxane bridges which exist on the silica surface heat-treated above 600 °C. It has been observed that an addition reaction of alkoxysilanes with Si-O-Si groups takes place on highly dehydroxylated silica when alkoxy and alkylsilane groups are formed on the surface.[128] Also, other side-reactions may occur on the silica surface, because evolved alcohol molecules may react with siloxane and silanol groups even at low temperatures.[103] According to the studies of Van der Voort et al.,[129] it is mostly the bridged hydroxyl groups of silica that are involved in the reaction with aminoalkoxysilanes in depositions from the liquid phase.

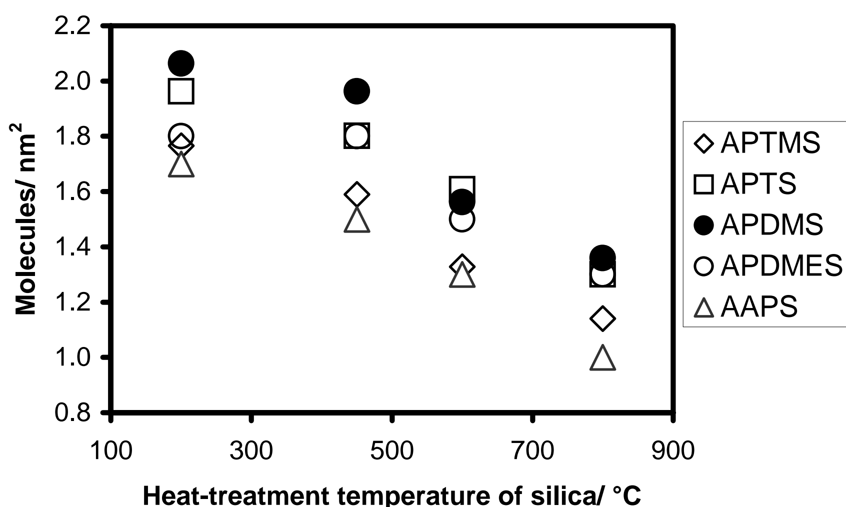



**Figure 14.** Surface densities of APTS, APTMS, AAPS, APDMS and APDMES on silica pretreated at various temperatures.[III,VII]

Comparison of the five precursors[I,VII] showed that the densest aminopropylalkoxysilane layer is achieved with bifunctional APDMS on silica heat-treated at 200 °C. The surface density is 2.1 molecules per $nm^2$ of silica. In the liquid phase, too, the highest amino group density has been achieved with a bifunctional aminosilane precursor.[130,131] However, almost the same surface density, i.e. 2.0 $N/nm^2$, is achieved with APTS on silica, and only a slightly smaller density with APTMS, APDMES, and AAPS molecules, viz. 1.7-1.8 $molecules/nm^2$. Thus, the

differences between precursors were, in fact, minor. The differences in the surface densities are due to the different sizes of the ligands and the size of the whole precursor molecule. Comparison of two precursors of different size, viz. AAPS and APTS, on the $SiO_2$ surface, clearly shows that the larger precursor molecule AAPS covers a greater surface area and overlaps more silanols on the surface than does the smaller molecule APTS (Figure 15).

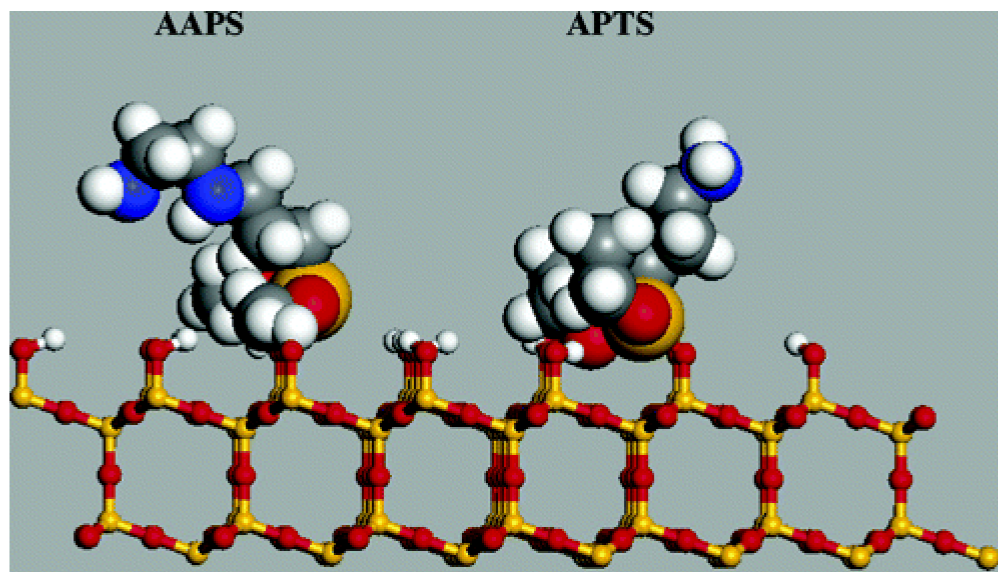



**Figure 15.** Relative sizes of AAPS and APTS molecules monodentately attached to the surface of β-cristobalite (111).[VII]

Greater differences in the surface densities of mono-, bi-, and trifunctional precursors have been observed in the liquid-phase depositions of silanes on silica. This is because bidentate and especially tridentate precursor molecules are hydrolyzed before deposition and give rise to polymer-structured multilayers. Thus, denser layers were obtained with trifunctional alkylchlorosilanes[132] and aminosilanes[130,131] than with monofunctional precursors. A surface density of 3.9 N/nm$^2$ was obtained when trifunctional APTS and bifunctional APDMS were deposited in an organic solvent on a planar substrate. A single surface-saturated molecular layer was achieved only with monofunctional APDEMS.[130,131]

#### 4.2.1.2 Effect of reaction temperature

As shown above, silica is saturated with vaporized aminopropylalkoxysilane molecules when deposition is at relatively low temperature, that is, near 150 °C. The effect of higher reaction temperatures, i.e. 200-300 °C, on the surface species on silica is discussed for trifunctional APTS,[III-V,VII] but APTMS and AAPS behave in a similar way. As can be seen in Figure 16,

mono- and bidentate bonding modes of APTS on silica appear in the $^{29}Si$ CP/MAS NMR spectrum as chemical shifts at $\delta=-53$ ppm and $\delta=-59$ ppm, respectively, regardless of the deposition temperature, i.e. 150-300 °C. In addition to the main reaction of the alkoxy groups with the silanols, the amino group is also observed to react with the surface, forming Si-N bonds. When the deposition temperature is raised from 150 °C to 300 °C, new peaks appear or small peaks increase in intensity in the $^{29}Si$ CP/MAS NMR spectra. At the reaction temperature of 150 °C, a completely new resonance appears at –40 ppm. This resonance has not been observed in the $^{29}Si$ NMR spectra of APTS samples deposited on silica from the liquid phase. The peak represents the region where the silicon atom of the silane molecule is surrounded by three unreacted oxygen atoms of ethoxy groups. Free APTS molecules are unlikely to be physisorbed onto the pores of silica at such a high reaction temperature and with subsequent nitrogen purging of any physisorbed molecules. The resonance of liquid APTS in deuterated chloroform ($CDCl_3$) in the solution-state $^{29}Si$ NMR spectrum is seen in the same region, viz. –45.4 ppm.[133] It seems likely, therefore, that APTS molecules are bound through the amino end of the molecule, while 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. Very faint peaks at the same positions are also seen at the deposition temperature of 150 °C. These bands and the above-mentioned band at –40 ppm are due to the reaction of amino groups with the ethoxy groups of APTS molecules on silica. One possible surface structure of APTS is shown in Figure 16; the others are depicted in publications IV and V.

In addition to reacting with the alkoxy groups, the amino groups were also observed to react with the silanol groups of silica. The presence of $O_3$-Si-N surface species, seen at approximately –80 to –90 ppm, confirms the reaction.[134] $O_3$-Si-N species are seen even at deposition temperature 150 °C, and more so at higher deposition temperatures, i.e. at 200 and 300 °C. Part of the $SiO_4$ species at about –100 to –110 ppm are then shifted to higher frequency due to the substitution of one oxygen for a nitrogen. The silanediol (i.e. geminal silanol), silanol, and siloxane groups on silica are generally seen in the $^{29}Si$ NMR spectra as broad peaks at –90.6, –99.8, and –109.3 ppm, respectively.[135]

Reaction of amino groups with the silica surface at 300 °C was further observed as the appearance of a new band in the N-H region of the DRIFT spectrum.[III] When the aminosilylated silica samples deposited at 300 °C were treated with water, the peaks due to

the Si-N bonds disappeared from both the $^{29}$Si NMR and DRIFT spectra. This is due to the sensitivity of Si-N bonds to hydrolysis.[134]

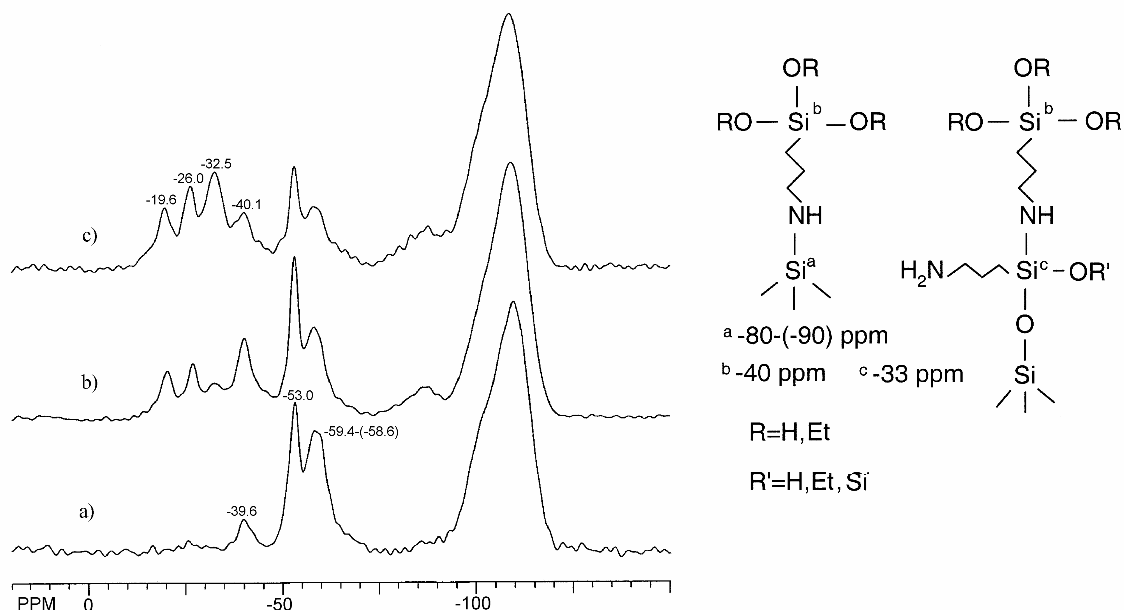



**Figure 16.** $^{29}$Si CP/MAS NMR spectra of APTS on silica pretreated at 600 °C after reactions at (a) 150 °C, (b) 200 °C, and (c) 300 °C. Some surface structures corresponding to selected peaks are shown.[IV,V]

The surface density of nitrogen and carbon atoms on silica after treatment with APTS clearly decreased when the deposition temperature was raised from 150 °C to 300 °C. Thus, as expected, the number of aminopropylsilyl groups on silica decreases at higher deposition temperature. Likewise, the carbon/nitrogen ratio decreased when the deposition temperature was increased, indicating that a larger number of ethoxy groups react or decompose on the surface at higher reaction temperature. The variation in the elemental concentrations of samples deposited at high temperatures also supports the assumption that decomposition of aminopropylsilanes on silica occurs. The O-H stretching band of free silanols in the DRIFT spectrum was observed for APTS deposited at 300 °C on silica, which also indicates decomposition of ethoxy groups and other surface structures on silica, as has been observed earlier for triethoxysilane, $HSi(OEt)_3$.[52] The existence of OH groups on the surface was further seen in $^1$H MAS NMR measurements. At deposition temperatures higher than 150 °C the deposition on silica is no longer ALD–type surface-saturated growth. Thus, the ALD window for aminopropylalkoxysilanes on silica is very narrow.

The reaction of the amino groups of bifunctional APDMS molecules with the ethoxy groups was not so clear because only a few ethoxy groups remain on the surface. However, the amino groups of APDMS molecules were also observed to react with the silica surface.

### 4.2.2 Deposition of a high-density aminopropylsiloxane network on silica

A high-density aminopropylsiloxane network on silica can be obtained by consecutive γ-aminopropylalkoxysilane/water cycles,[VI,VII] as shown in Figure 17. This procedure was found suitable for trifunctional precursors such as APTMS, APTS, and AAPS, which react with silica leaving free alkoxy groups on the surface. Hydrolysis of these alkoxy groups during the water purge results in the formation of hydroxyl groups. The sequential increase and decrease in the number of carbon atoms per $nm^2$ of silica pretreated at 450 °C during aminosilane/water cycles are clearly seen in Figure 18. The same pattern was seen in the DRIFTS and $^{13}C$ CP/MAS NMR spectra. The largest increase in the number of nitrogen groups on silica occured during the first cycle, but the number increased further during the next four cycles. The fifth and sixth aminosilane/water cycles no longer had a distinct effect on the nitrogen content. After four cycles, surface densities up to 3.0 were achieved for APTMS and APTS/$nm^2$ on silica pretreated at 450 °C. With the AAPS precursor, a surface density of 2.7 molecules/$nm^2$ was achieved. The lower density for AAPS than for APTMS or APTS is due to the larger size of the molecule, as discussed above.

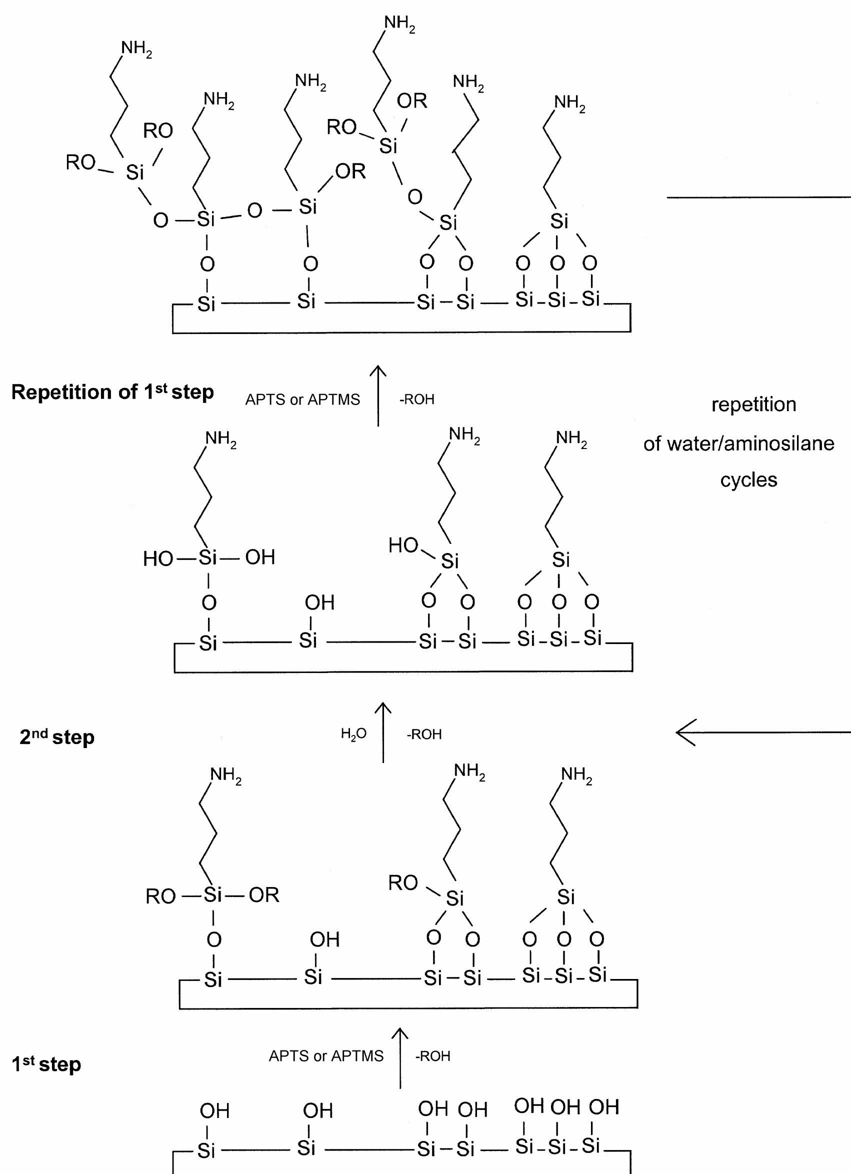
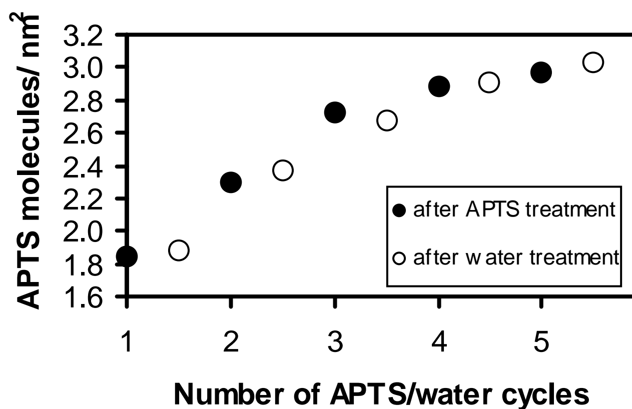



**Figure 17.** Stepwise deposition of a high-density aminopropylsiloxane network on silica.[VI]



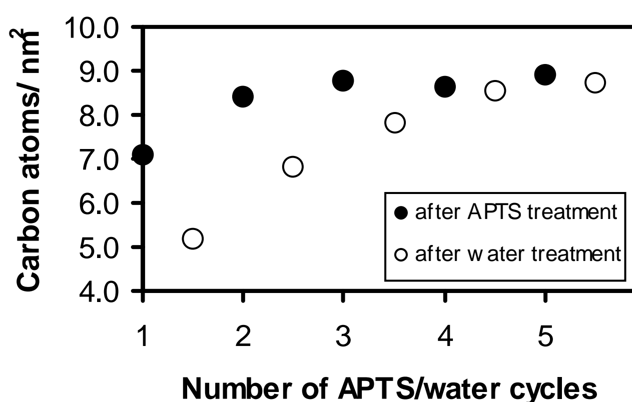




**Figure 18.** Effect of APTS/water cycles on the surface density of APTS molecules (above) and carbon atoms (below) on silica pretreated at 450 °C.[VI]

After four aminosilane/water cycles, all silanols were reacted and the surface was saturated, and the maximum amino group density was achieved. Thus, the repetition of these cycles resulted in the formation of a high-density aminopropylsiloxane network, which is assumed to grow through horizontal polymerization of silane molecules as a result of the saturation achieved. An idealized scheme of a dense amino-terminated siloxane network is shown in Figure 19 where one nm$^2$ of silicon dioxide surface containing approximately five silanol groups has reacted with three aminosilane molecules. The planar surface shown in Figure 19 is a simplified scheme of the silica surface heat-treated at 450 °C. In reality, only half of the OH groups are isolated and the other half hydrogen-bonded, and all hydroxyl groups do not react. A molecular model of the aminosilylated silicon dioxide surface[VI,59-60] suggests that the maximum number of amino groups is ca. 3.0 per nm$^2$, as was also observed in the experimental results. Thus, a monolayer was successfully deposited on silica with the present method.

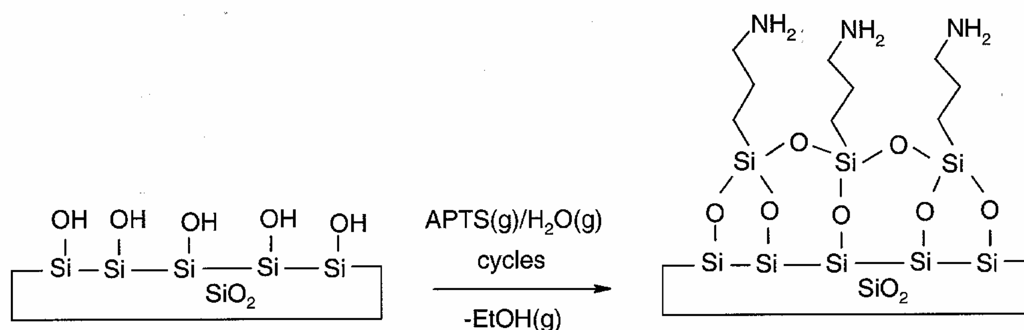



**Figure 19.** Aminopropylsiloxane network on one $nm^2$ of silica.[VI]

## 4.3 Growth of organic multilayered polyimide structures on amino-functionalized silica

A number of organic precursors that can be vaporized at low temperatures without decomposition can be used to deposit organic multilayered structures onto porous or planar surfaces by ALD. As an example of the deposition of these structures on porous silica, the formation of polyimide structures on aminosilylated silica is illustrated below (Figure 20). According to elemental analyses (Table 6) and DRIFT spectra (Figure 21), the organic precursors, pyromellitic anhydride (PMDA) and diaminohexane (DAH), are deposited on aminosilylated silica without significant decomposition. With the deposition of PMDA the surface density of the nitrogen atoms stays constant, but the surface density of the carbon atoms increases. At the same time, the C-H vibrations of the aromatic ring of PMDA are seen above 3000 $cm^{-1}$ and the change in the chemical environment of N-H bonds is evident from a broad peak appearing at 3660-3300 $cm^{-1}$. Deposition of DAH on PMDA/APDMS/$SiO_2$ causes a clear increase in the surface density of nitrogen. The peaks in the DRIFT spectra are not discussed here in detail, but will be treated in a forthcoming paper.[136]

The results show that the deposition of multilayered structures, starting from the deposition of the aminopropylsiloxane network, is fully feasible with ALD. Organic self-assembled superlattices have earlier been deposited on the planar $SiO_2$ surface by Burtmann et al.,[3,4] who prepared aminosilylated $SiO_2$ surfaces in the liquid phase and the actual polyimide layers in the gas phase by MLD.

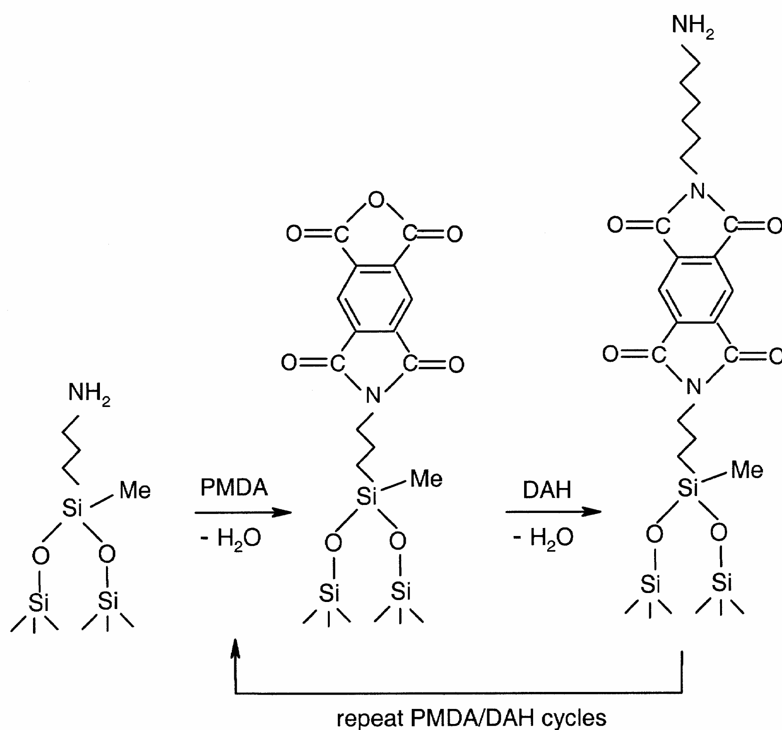



**Figure 20.** Deposition of pyromellitic anhydride (PMDA) and diaminohexane (DAH) on APDMS -treated silica surface, resulting in the formation of polyimide structures.

**Table 6.** Results of elemental analyses after deposition of polyimide structures on silica heat-treated at 600 °C.

| Structure | N atoms/ $nm^2$ | C atoms/ $nm^2$ | Determined C/N ratio | Theoretical C/N ratio |
|---|---|---|---|---|
| APDMS/$SiO_2$ | 1.4 | 6.6 | 4.7 | 4 |
| PMDA/APDMS/$SiO_2$ | 1.3 | 13.2 | 10.0 | 14 |
| DAH/PMDA/APDMS/$SiO_2$ | 2.0 | 14.8 | 7.4 | 6.7 |
| PMDA/DAH/PMDA/APDMS/$SiO_2$ | 2.0 | 16.4 | 8.2 | 10 |

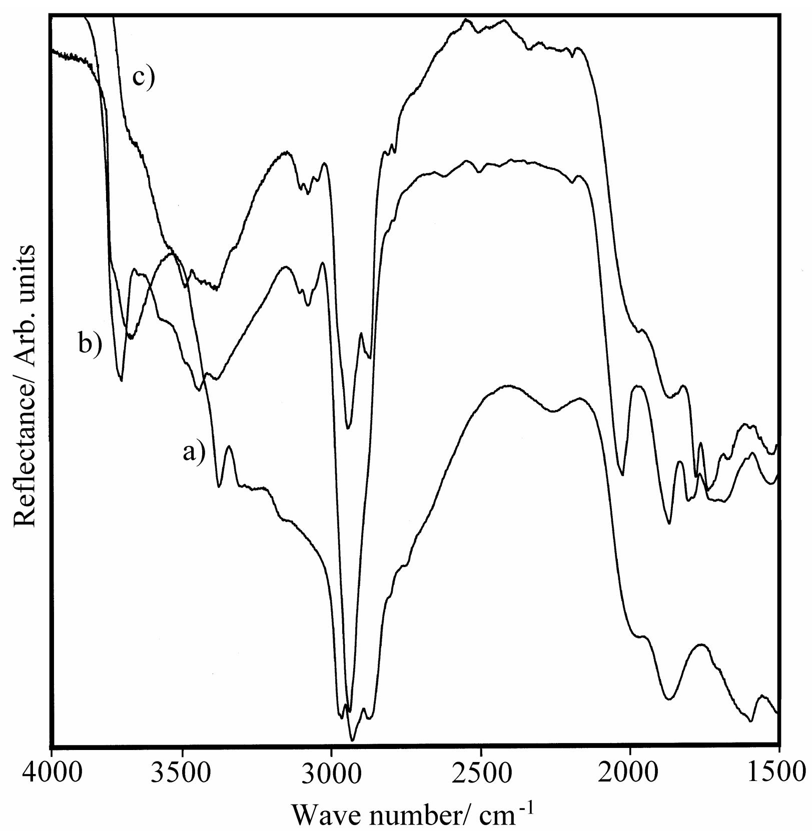



**Figure 21.** DRIFT spectra of (a) APDMS on silica pretreated at 600 °C, (b) PMDA/APDMS/$SiO_2$, and (c) DAH/PMDA/APDMS/$SiO_2$.[136]

## 5. CONCLUSIONS

Because ALD growth is based on the surface reactions of precursor molecules with a substrate, characterization of the surface species on porous substrates is very important. TG, DRIFTS/PLS, and $^1$H MAS NMR were found to be accurate techniques for the characterization of the surface species. With all these methods, not just the surface silanol groups but also the bulk internal silanols on silica are determined. While TG offers a relatively fast and simple method for the quantification of the total number of silanol groups, the numbers of different types of silanols cannot be determined. Combined DRIFTS/PLS method also allows the determination of the total number of silanol groups. Once calibration has been performed DRIFTS/PLS offers a fast analytical method, that can easily be applied to numerous kinds of samples in process analysis, for example. The advantage of $^1$H MAS NMR is the quantification of both isolated and hydrogen-bonded silanol groups on silica. It is, however, time-consuming and expensive.

The present study showed that amino-functionalized silica surfaces can be prepared by ALD without solvent in a simple, conformal, and reproducible manner. Volatile aminopropyl-alkoxysilanes studied can be used as precursors because they do not decompose during vaporization or subsequent deposition. The reaction temperature affected the surface species on silica so that the use of relatively high reaction temperatures, i.e. 150-300 °C, led to side-reactions between the amino groups of bi- and trifunctional precursors and silanols groups or alkoxy groups of other precursor molecules on silica. Thus, deposition temperatures less than 150 °C (under pressure of 2-5 kPa) should be used to avoid side-reactions. The deposition and characterization of a single surface-saturated molecular layer on the surface allows study of various surface structures on porous substrates. The number of adsorbed precursor molecules (and terminal amino groups) on silica could be controlled between 1.0 and 3.0 molecules (or $NH_2$ groups/nm$^2$) through heat-treatment of silica (200-800 °C), choice of the precursor (APTMS, APTS, AAPS, APDMS, APDMES), and the number of reaction cycles (from 1 to 4) of gas-phase reactions of aminopropylalkoxysilane precursor and water. Such control is not possible with the liquid-phase methods currently applied to the preparation of amino-functionalized silica surfaces. The highest amino group density was achieved with the bifunctional precursor, APDMS, on silica pretreated at 200 °C when a single surface-saturated molecular layer was deposited. Still higher amino group densities were obtained when sequential reactions of trifunctional APTMS, APTS or AAPS, and water were applied. A

high-density aminopropylsiloxane network, which can be considered as a monolayer, could be deposited on silica because the surface was observed to be saturated with the precursor molecules. The results obtained from these experiments on porous substrates can further be applied to planar substrates, and valuable information on the surface chemistry and deposition process on surfaces can be obtained.

As shown in this work, ALD enables a controlled deposition of functionalized surfaces, in addition to the oxides, sulfides, and nitrides earlier deposited on porous supports for catalyst applications. It was also shown that even more complex organic layers, such as polyimides, could be deposited on functionalized surfaces. In the present study polyimide structures were deposited on aminosilylated silica using PMDA and DAH as precursors. Low temperatures are especially desired to prevent decomposition of organic precursors. Pressure within the ALD reactor should be as low as possible, so as to provide the lowest vaporization and deposition temperatures. In addition to the present ALD applications, ALD has great potential for industrial applications in the future in completely novel areas where organic layers may be applied to planar or porous substrates.

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