Effects of heat-treatment of silica and precursor on the surface density of aminosilanes deposited onto silica by ALD

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Amino-terminated molecular layers on silicon dioxide surfaces are widely used as coupling agents. Amino-functionalized surfaces are frequently utilized in chromatography, catalyst technology, biochemistry and electronics, for example (1). Amino-terminated layers can be obtained by binding aminopropylalkoxysilanes onto the solid surface. The preparation of aminosilane-modified surfaces is most often carried out in the liquid phase. Nevertheless, the surface-controlled gas-phase deposition, ALD (atomic layer deposition) (2), eliminates many of the tedious operations of the liquid-phase technique, such as controlled hydrolysis of alkoxysilanes, solvent removal and recovery, washing procedures and other manipulations (3). In addition, a very reproducible product can be achieved by ALD.

In this work, we have studied the gas-phase modification of porous silica with four precursors: γ-aminopropyltrimethoxysilane (APTMS), γ-aminopropyltriethoxysilane (APTS), γ-aminopropyldiethoxymethylsilane (APDMS) and γ-aminopropyldimethylethoxysilane (APDMES). Surface-saturated layers of aminosilanes were deposited on silica at a low reaction temperature, i.e. 150 °C, and at a pressure of 20-50 mbar. When aminosilanes are attached onto the silica surface a sharp peak due to stretching vibration of free OH groups at 3748-3740 cm^{-1} disappears in the DRIFT spectrum (Fig. 1). At the same time bands corresponding to IR -vibrations for N-H and C-H bonds appear in the spectra. In addition, a broad band for unreacted silanol groups hydrogen-bonded to alkoxy groups is seen in the DRIFT spectra at 3740-3500 cm^{-1}. At high pretreatment temperatures of silica strained siloxane bridges are assumed to be opened and reacted with aminosilanes.

The effect of heat-treatment temperature of silica on the achieved surface density of aminosilanes was studied on silica pretreated at 200-800 °C on the basis of elemental analyses. The pretreatment temperature of silica was observed to have a distinct influence on the surface density of aminosilanes (Fig. 2, Tables 1 and 2). The surface densities decreased from 1.8-2.1 amino groups/nm^2 to 1.1-1.4 amino groups/nm^2 when the pretreatment temperature of silica was increased. The most dense moelcular layer was achieved with APDMS on silica heat-treated at 200 °C. However, the differences between the precursors were not large considering the surface densities achieved.

1. Vansant, E.F., Van Der Voort, P., Vrancken, K.C., *Characterization and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam 1995, Ch. 8.
2. Ritala, M., Leskelä, M., in *Handbook of Thin Film Materials*, Ed. H.S. Nalwa, Vol.1., Academic Press, San Diego 2002, pp. 103-159.
3. Scott, R. P. W. in *Silica Gel and Bonded Phases*, John Wiley & Sons Ltd., Chichester 1993, pp. 139-174.

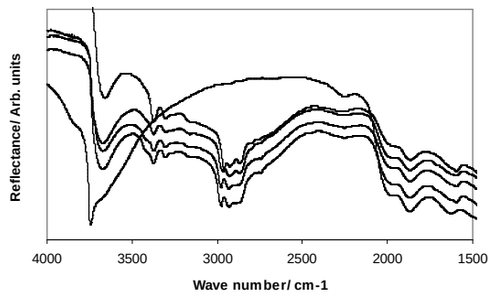

Fig. 1. DRIFT spectra of silica heat-treated at 450 °C and APTMS, APTS, APDMS, APDMES –modified silica (from below upwards).

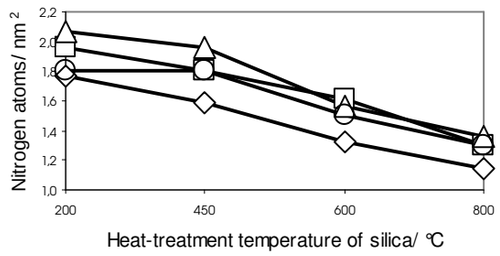

Fig. 2. Effect of heat-treatment and precursor on the surface density of aminosilanes; ◊= APTMS □= APTS Δ= APDMS o= APDMES.

Table 1. Results of elemental analyses for aminosilane - modified silica.

	APTMS		APTS	
Heat-treatment of silica / °C	N atoms/ nm^2	C atoms/ nm^2	N atoms/ nm^2	C atoms/ nm^2
200	1.8	7.5	2.0	7.3
450	1.6	7.3	1.8	6.9
600	1.3	7.1	1.6	7.3
800	1.1	5.9	1.3	5.3

Table 2. Results of elemental analyses for aminosilane - modified silica.

	APDMS		APDMES	
Heat-treatment of silica / °C	N atoms/ nm^2	C atoms/ nm^2	N atoms/ nm^2	C atoms/ nm^2
200	2.1	7.9	1.8	7.8
450	2.0	6.8	1.8	8.2
600	1.6	6.9	1.5	7.4
800	1.4	6.5	1.3*	6.3*

* heat-treatment of silica was performed at 820 °C instead of 800 °C.