Microporous and Mesoporous Materials xxx (2016) 1–11

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Water-based functionalization of mesoporous siliceous materials, Part 1: Morphology and stability of grafted 3-aminopropyltriethoxysilane

Frank Bauer [a], [*], Saskia Czihal [a], Marko Bertmer [b], Ulrich Decker [c], Sergej Naumov [c], Susan Wassersleben [a], Dirk Enke [a], [**]

[a] *Institute of Chemical Technology, Universität Leipzig, D-04103 Leipzig, Germany*
[b] *Institute of Experimental Physics II, Universität Leipzig, D-04103 Leipzig, Germany*
[c] *Leibniz Institute of Surface Modification, D-04318 Leipzig, Germany*

ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form
16 January 2016
Accepted 25 January 2016
Available online xxx

Keywords:
Biogenic silica
Modification
3-Aminopropyltriethoxysilane
^{29}Si NMR spectroscopy
DFT calculations

ABSTRACT

Surface modification of mesoporous biogenic silica (rice husk ash) by aqueous and ethanol-based 3-aminopropyltriethoxysilane (APTES) grafting solutions has been investigated using ^{29}Si NMR, ESI-MS, TGA, surface-sensitive NH_2 titration, and DFT method. Prior to grafting, a rapid formation of ladder-like aminosilane oligomers has been observed in both solvents limiting the grafting time for the mostly desired formation of a monomolecular organosilane layer to few minutes. An excess of water yielded a long-term stable equilibrium between the oligomerized APTES species within the grafting solution promising a reproducible surface modification. After curing at 120 °C, washing studies showed that these oligomeric aminosilane clusters have been successfully grafted but yielding a heterogeneous surface morphology with even pore blocking rather than a dense, uniform aminosilane monolayer.

In addition, the optimized structures of three different grafting modes between APTES and a silica cluster model were obtained by DFT calculations. The results indicated that bond lengths and angles of the different grafting modes reveal no substantial structural distortions. Nevertheless, the ladder-like grafting mode is given preferential consideration because the DFT results are in accordance with the ESI-MS and ^{29}Si NMR findings.

1. Introduction

For the preparation of organic-inorganic composite materials, coupling agents such as the very versatile organo-substituted trialkoxysilanes are commonly used to accomplish a durable molecular bridge between the polymeric matrix and the inorganic reinforcement. In addition, these bifunctional organosilanes can be used as "primer" molecules providing an anchorage point on the surface of oxide particles and a linkage for the immobilization of different kinds of biomolecules such as enzymes [1], dyes [2–4], and metal nanoparticles [5]. Thus, surface functionalization of silica fibers [6,7], silica nanoparticles [8,9], ordered mesoporous materials [10], porous glasses [11], and biosilica materials [12] by various trialkoxysilanes is a crucial issue for their numerous industrial, biological, and environmental applications. Furthermore, the stability of the grafted trialkoxysilane layer on the inorganic surface is an important question for the success of multi-step functionalization reactions and the long-term stability of composite systems. At this point it has to be mentioned that in case of modern photochemistry relatively large dye molecules derived from azobenzene/stilbene [13] and perylene [14] have been firmly incorporated only by adsorptive forces into molecular sieves such as $AlPO_4$-5, ZSM-5 and zeolite L. For the large-pore zeolite L having one-dimensional channels of 12-membered rings with channel openings of 0.71 nm in diameter, however, arising dye leakage could only be strictly avoided by sealing the pore aperture with a polymer coating [15]. But, the effectiveness of such sealing techniques is highly questionable for many other macro/meso-porous systems, but most important for all non-porous host materials. Therefore, chemical anchoring of active guest components onto the surface of inorganic host systems is the base of many composite applications and a permanent interest on the morphology of each individual molecular bridge within new (but also properly investigated) hybrid materials seems to be justified.

---

[*] Corresponding author. Tel.: +49 341 9736300; fax: +49 341 9736349.
[**] Corresponding author. Tel.: +49 341 9736302; fax: +49 341 9736349.
E-mail addresses: frank.bauer@uni-leipzig.de (F. Bauer), dirk.enke@uni-leipzig.de (D. Enke).

http://dx.doi.org/10.1016/j.micromeso.2016.01.046

Please cite this article in press as: F. Bauer, et al., Water-based functionalization of mesoporous siliceous materials, Part 1: Morphology and stability of grafted 3-aminopropyltriethoxysilane, Microporous and Mesoporous Materials (2016), http://dx.doi.org/10.1016/j.micromeso.2016.01.046

Among the organosilanes, aminosilanes (in particular 3-aminopropyltriethoxysilane (APTES)) are of special interest owing to the reactive amino group and their outstanding water solubility which significantly facilitates the application of any surface modification reaction on an industrial scale. Accordingly, considerable effort has been spent on optimizing silanization conditions in aqueous and non-aqueous solutions [16–18] early on and is still invested in this fundamental field [19–21]. The main objectives of such studies are the influence of silane concentration, water content, pH value, type of auxiliary solvent, temperature, reaction time, and drying/curing conditions on silane surface density and stability as Zhu et al. [22] recapitulated in their work on aminosilane-derived layers on silica.

The two classical mechanisms for surface modification by trialkoxysilanes involve: (i) a one-step solvolysis reaction under exceptionally water-free conditions and (ii) a two-step reaction via (partial or total) hydrolysis of the silane agent to the various intermediate organosilanols followed by condensation reactions with surface OH groups and/or neighboring silanols. While trace quantities of water can most likely be avoided in gas-phase reactions, it is difficult to exclude hydrolysis of alkoxysilanes in solutions even when working in dry solvents because water molecules are efficiently adsorbed on hydrophilic oxide surfaces [22]. On the other hand, excess water is reported to result in both uncontrolled lateral/vertical crosslinking of silane molecules on the surface [23–25] and formation of silane oligomers within the grafting solution [26,27], which can also react with and attach to the surface. This polymerization problem of hydrolyzed trialkoxysilanes is associated with the ability of organosilanols to interact also with silanols of neighboring organosilane molecules, which give rise to a number of linear, branched, and cyclic siloxane structures. In addition to such disordered layers of oligomeric organosilanes, the self-condensation of trialkoxysilanes grafted in form of ladder-like structures has been reported [28,29]. Using a modified LC-MS technique, Beari et al. [26] observed siloxanes with up to nine SiO units formed within a 10% aqueous solution of APTES. Obviously, the covalent attachment of such polycondensed organosilanes (similar to silsesquioxanes) results in a heterogeneous surface morphology and it may significantly influence the application of the modified surfaces.

For investigating the molecular structure of grafted trialkoxysilanes with ^{29}Si NMR spectroscopy, unfortunately, there is uncertainty with regard to the assignments of signals (Fig. 1). But, the relative abundance of the various silane species formed within the grafting solution and/or in surface-near interphase layer obviously controls the structure and morphology of the subsequent silane deposits on the surface. To gain more insight into the composition of eco-friendly aqueous APTES grafting solutions, this work on surface modification of rice husk ash (RHA) combines ^{29}Si NMR spectroscopic studies with ESI-MS measurements. After curing and washing, the APTES-modified RHA samples have been characterized by sorption measurements, CHN analysis, thermogravimetry, ^{29}Si CP MAS NMR, and surface-sensitive NH_2 titration. In addition, quantum chemical calculations were performed to obtain a more indicative image of the different APTES grafting modes rather than given by the schematic representations.

2. Experimental methods

2.1. Materials

Rice husk ash (RHA) used in this study has been prepared due to a protocol of Alyosef et al. [30] including hot acid leaching of rice husk prior to burning at 600 °C. The samples were composed of 99 wt.% SiO_2 and showed less than 0.1 wt.% carbon. SEM pictures of the siliceous material derived from RHA, as was demonstrated earlier by Alyosef [30], reveal its biological origin as well as intraparticle meso/macropores with diameters between 40 and 60 nm (responsible for the remarkably high specific surface area of the treated RHA material) and additional macropores in the range of 300 and 500 nm. To increase the density of OH surface groups, the burnt RHA samples has been hydrothermally treated at 120 °C for 2 h using a Teflon autoclave and finally dried at 120 °C overnight. To obtain a silane surface concentration of one molecule 3-aminopropyltriethoxysilane (APTES, obtained from Sigma–Aldrich) per nm^2, a certain amount of APTES (depending on the specific RHA surface after rehydroxylation) was dissolved in water, ethanol, and an ethanol/water mixture. The solvent ethanol (analytical grade, AnalaR NORMAPUR) contains max. 0.2% water. After solvent evaporation, the modified RHA samples were dried at 120 °C overnight. Finally, the functionalized RHA has been washed three times with the same solvent used in the grafting process.

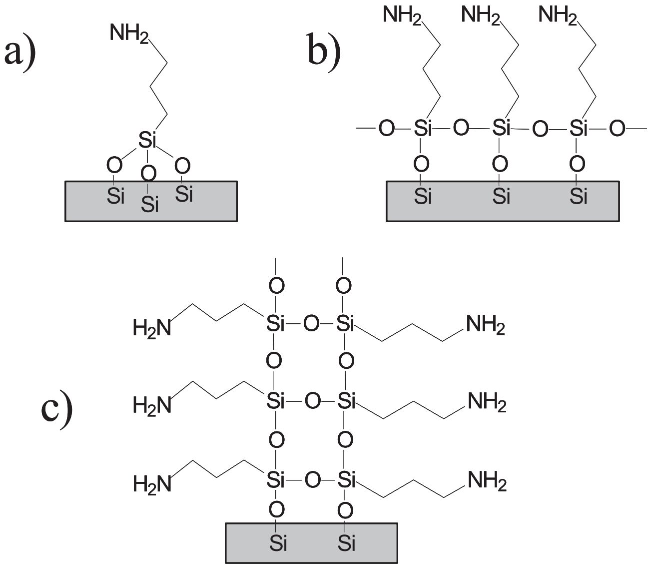

Fig. 1. Schematic representation of covalently bonded APTES on silica surfaces: (a) tridental grafting of aminosilane, (b) linear cross-linked oligomeric aminosilanes, and (c) latter-like arranged oligomeric aminosilanes; all of these structures may be responsible for dominating T^3 signals observed in ^{29}Si MAS NMR spectra.

2.2. Characterization techniques

The hydrolyzed and partially condensed APTES was characterized by NMR and MS spectroscopy. High-resolution ^{1}H NMR and ^{29}Si NMR spectra were recorded using a Bruker Avance-600 II+ spectrometer (Germany). Deuterated water and methanol were used as solvents. Especially, the ^{29}Si NMR spectroscopy gives useful information on the coordination at the Si atom of trialkoxysilanes (T^i signals) as well as of Si atoms of the silica material (Q^i signals) [8]. The percentages of the ^{29}Si species were determined by signal integration and thus, the extent of silane hydrolysis (T^0 signals) and the different steps of silane condensation reactions (T^1, T^2, and T^3 signals) have been estimated. The active silanol reactivity (SR) of the grafting solution were calculated according to $SR = (3\ T^0 + 2\ T^1 + 1\ T^2)/3$ assuming that T^3 structures do not contribute to SR because they do not bear any silanol groups [26]. Using standard ionization conditions and recording the positive ions, ESI-MS spectra of the grafting and washing solutions were measured on a Bruker Daltonics Esquire 3000+ spectrometer (Germany). The content of aminosilanes within the washing solutions has been

Please cite this article in press as: F. Bauer, et al., Water-based functionalization of mesoporous siliceous materials, Part 1: Morphology and stability of grafted 3-aminopropyltriethoxysilane, Microporous and Mesoporous Materials (2016), http://dx.doi.org/10.1016/j.micromeso.2016.01.046