



Mixed bifunctional surface-modified silicas using tethered aminofunctional silane catalysts



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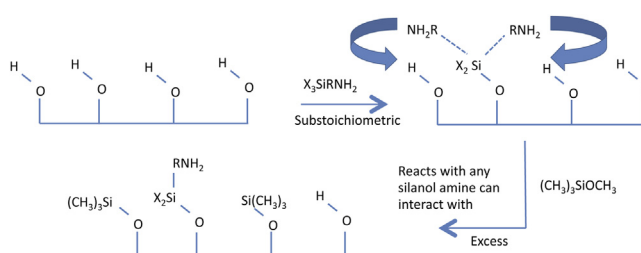
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HIGHLIGHTS

- A new way to prepare bifunctional surface modified silicas is presented.
- Bifunctionality was achieved at the molecular level.
- Hydrophilic and hydrophobic surface groups are intimately mixed on the surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Amines are known to catalyse silica surface reactions with alkoxy functional organosilanes. In this work, a substoichiometric amount of an aminofunctional silane is bound to the silica surface by reaction with available silanols. This surface bound amine is used to catalyse the reaction of nearby silanols in its vicinity. The result is a bifunctional modified silica surface with two different functional groups intimately mixed at the molecular level. Three types of silicas were modified with a substoichiometric amount of different aminofunctional silanes possessing various structures. These amino-modified silica surfaces were then exposed to a relatively unreactive alkylsilane that requires the presence of an amine for catalysis of the surface reaction. Select materials were characterized by FTIR, TGA, as well as ²⁹Si and ¹³C solid state NMR. Elemental analysis data was obtained for all materials after aminosilane reactions and after alkylsilane reaction, with and without the presence of surface bound aminosilane present, for quantitative analysis. Each surface bound aminosilane catalyses the reaction of approximately one alkylsilane. An aminosilane that is bound with one bond to the surface catalyses a greater number of alkylsilanes per aminosilane. Surface modified aminosilanes on nanoparticulate fumed silica on average catalyse a greater number of alkylsilanes compared to silica gels. This is the first report demonstrating the feasibility of using a surface bound aminosilane as a catalyst to synthesize intimately mixed bifunctional silica surfaces.

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1. Introduction

1.1. Uses

Silica surfaces modified with organosilanes have found use in a variety of applications such as, for example, adsorption of heavy metal ions from aqueous solution, separations media, and supports for heterogeneous catalysis [1–5]. The organosilane provides useful, tunable, surface properties to the silica for a given

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application by the organic group's chemical structure based on alkyl chain length variations and/or functional group properties. While the vast majority of work has been done reacting a surface with a single organofunctional silane, potentially more versatile materials might be synthesized if more than one organosilane is used to modify the surface. Certainly this idea is not novel and has been reported for unique bonded phases for separation media [6–8], biofilm synthesis [9], and a novel approach for multifunctional mesoporous materials [10]. Iwasawa and coworkers have modified acidic silica–alumina surfaces with basic aminosilane functional groups with different structures, often using the unreacted surface groups as the second or third functional group [11–13]. Surface modified silicas very similar to those discussed here have also been used in the manufacture of toners [14]. However, precise control of the location of surface reaction on the external surface of a particle is more of a challenge.

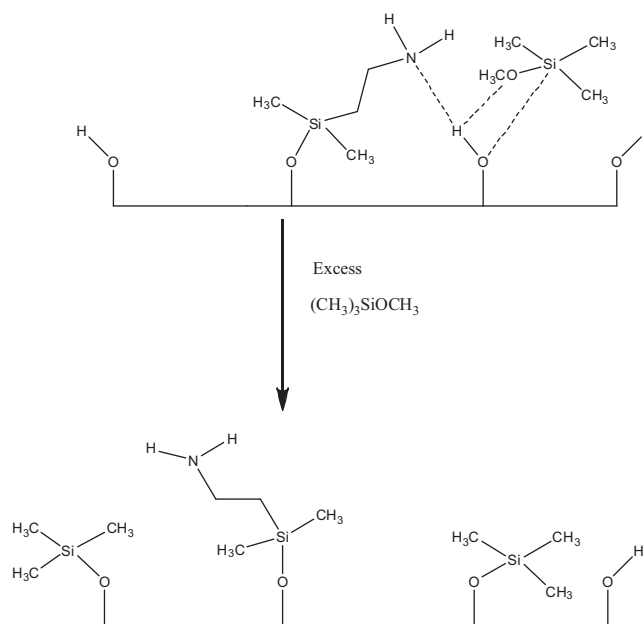
1.2. Possibilities for bifunctional surface modification

In the extreme one can envision two very different types of particles resulting from surface modification of two (or more) reactants. The first is a directional modification where, for instance, one hemisphere is reacted with one type of organosilane and the other hemisphere reacted with a second organosilane with different properties. Such so-called Janus particles have been recently synthesized resulting in fascinating materials [15–17]. The second type of material is where a homogeneous, molecular level mixing of organosilane on the silica surface is guaranteed by the synthetic procedure. Although one might consider a simple 2-step process where first a sub-stoichiometric amount of one organosilane is reacted with available silanols, followed by a second reaction with a different organosilane, there is no control over where the second organosilane would react beyond the fact that it would react with the remaining silanols, wherever they may be accessible. Here we describe a method where the second organosilane will react in close proximity to where the first organosilane is immobilized.

1.3. Approach

While many organofunctional silanes are not particularly reactive with silica surface silanols, amine compounds act as useful catalysts to facilitate these surface reactions. The basic amine interacts with the acidic silanol proton, increasing the nucleophilicity of the surface oxygen thus increasing its reactivity [18,19]. This explains why organosilanes containing an amine functional group are highly reactive with silica surface silanols, although they apparently do not autocatalyse their own reaction with the silanols [20]. However once an aminofunctional silane is immobilized onto a silica surface, the amine group should catalyse reactions of other (nonreactive) organofunctional silanes with nearby silanols. As long as the amine can interact with nearby silanol protons, those silanols will be activated and susceptible to reaction with other organofunctional silanes that require the amine catalyst to react. This is shown in Scheme 1.

In this scheme it can be seen that the aminosilane can interact with either of the silanols to its “left” or its “right”, and catalyse a surface reaction with the alkylsilane. However one silanol in the scheme is out of the anchored amine group's reach and does not react. Note that when a silica surface is modified with less than a stoichiometric amount of aminosilane ($\alpha_{\text{OH}} < 1$), as long as there exist silanols that can interact with the amine group, those surface groups are susceptible to reaction. This produces a molecular level dispersion of mixed bifunctional surface oxide. The combination of a hydrophilic amine in close proximity to a strongly hydrophobic trimethylsilyl functional group provides the opportunity to explore potentially unique properties of these synthesized materials.



Scheme 1. The surface bound aminosilane shown can interact with two adjacent silanols thus catalyzing those silanols' reaction with the less reactive trimethylmethoxysilane. The silanol that is too distant from the aminopropyl group to interact remains unreacted.

In this report we intend to show that the concept illustrated and explained above is valid. In addition the role of aminosilane structure, and the effects of silica textural factors and their interplay will be explored. Different aminosilanes will be used, containing one or three hydrolysable alkoxy groups. The scheme above illustrates the reaction of silica with an aminosilane containing one hydrolysable group. With three hydrolysable groups an aminosilane might react with two surface silanols, potentially restricting the movement of the aminoalkyl group, or possibly with other aminosilanes resulting in cross-linking. Other aminosilane structural factors include alkyl chain length (propyl, butyl), and diamino versus a single amino group per molecule. The amino functional silanes will be reacted with three different silicas having varying textural properties. Two are commercially available porous silica gels possessing widely different pore radii and volumes; the third is a fumed silica consisting of solid, primary nanoparticles. The porosity and overall textural characteristics of the latter material is dependent on the aggregation behavior of the primary nanoparticles, which can change depending on a variety of external factors.

2. Materials and methods

2.1. Materials

Silica gel HP39 “wide pore” and 200DF “narrow pore” samples were donated by Crosfield (Chicago, IL). Fumed silica HS-5 was donated by the Cabot Corporation (Tuscola, IL). Organofunctional silanes (>98%) were obtained from Gelest, Inc., Morrisville, PA, and used as received. The list of organosilanes includes 3-aminopropyltrimethylethoxysilane (APDMES), N-2-aminoethylisobutyldimethylmethoxysilane (AEIDMS), 3-aminopropyltriethoxysilane (APTES), 4-aminobutyltriethoxysilane (ABTES), and trimethylmethoxysilane (TMMMS). Structures of the aminosilanes and their abbreviations are provided in Table 1.

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