

Functionalization of silica surfaces with mixtures of 3-aminopropyl and methyl groups

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Abstract

The surface of mesoporous M41S silica material was functionalized with 3-aminopropyl and methyl groups and with mixtures of both. The ratio of the two groups on the silica surface could be adjusted by changing the molar ratio of the corresponding alkoxy-silanes in the reaction mixture. The fraction of 3-aminopropyl on the surface was always larger than in the functionalization reaction mixture. Moreover, functionalization with the 3-aminopropyl group or with mixtures of the 3-aminopropyl and methyl groups led to higher molar coverages of the silica surface than functionalization with the methyl group alone. One reason for these effects is that the amino group base-catalyzes the hydrolysis of the alkoxy-silanes and thereby enhances the reaction of the silanes with the silica surface. The 3-aminopropyl/methyl-functionalized materials showed a very high stability against hydrolysis in boiling water because the siloxane bonds of the silica framework were protected by the organic moieties.

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1. Introduction

The surface of silica materials can be functionalized with various organic moieties, by reaction of the silanol groups on the silica surface with chloro- and alkoxy-silanes [1]. Many different silanes with a large variety of organic moieties are commercially available for that purpose. The most important commercial application of functionalized silicas is as stationary phases for chromatography [1]. The methodology of surface functionalization is, however, applicable to all silica surfaces, independent of the porosity of the starting material. Therefore it is not surprising that the discovery of ordered mesoporous silica materials [2] kindled much interest in the surface functionalization of these materials. It was shown that functionalization of ordered

mesoporous materials can induce very interesting new properties due to the ordered structure of the pores [3,4].

An organic group which is often used for functionalization is 3-aminopropyl. A primary amine is a good ligand for metal ions and can therefore serve as sorbent in waste water treatment [5,6] or can immobilize catalytically active transition metal ions [7–9]. Furthermore, the nucleophilic primary amine can be used as linker between the silica surface and any organic species with a leaving group for a nucleophilic substitution reaction [10–15] or serve as a solid base catalyst [10,16–19]. Mesoporous materials functionalized with 3-aminopropyl groups can either be prepared by co-condensation of 3-aminopropyl-trialkoxysilane with a silica precursor (typically TEOS) [20,21] or by post synthetic grafting on the surface of a mesoporous silica support. An important advantage of post synthetic grafting is that the mesoporous silica can be calcined to remove all template. The calcination stabilizes the silica framework. Moreover, the synthesis of the support and the

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functionalization are independent, which allows more flexibility in both procedures. Therefore functionalization by post synthetic grafting was investigated in this study.

As mentioned before, silica materials functionalized with 3-aminopropyl groups have diverse potential applications. Still these materials often suffer from poor hydrothermal stability in humid environment or aqueous solutions. The reason is that all silica-based materials tend to hydrolyze under basic conditions. Therefore 3-aminopropyl-functionalized silica materials are often not stable enough for technical processes. One approach to overcome this limitation is to functionalize the silica surface with a second group which protects the surface against unwanted hydrolysis. It was reported for example that a silica surface, that was functionalized with a mixture of chloropropyl and methyl groups, was hydrothermally more stable than materials functionalized with chloropropyl alone [22]. We therefore functionalized mesoporous M41S materials with mixtures of 3-aminopropyl and methyl groups (see Refs. [23–25] for other examples of mixed functionalization of silica surfaces). This methodology also allows to adjust the amount of active 3-aminopropyl species on the surface. This is especially important for applications in which a defined chemical environment on the surface is more important than the maximal number of functional groups, as is often the case in heterogeneous catalysis. The functionalization method presented hereafter was developed from the method described by Feng et al. [4] and our group [26].

2. Experimental

2.1. Synthesis procedure

All chemicals were obtained from Fluka and used as received. A pure silica mesoporous material was used as support for all functionalization reactions. Experimental details including a profound characterization were presented elsewhere [27]. This silica material has mesopores with uniform pore diameters but no long range order. The synthesis procedure is based on the method described by Beck et al. [2] and the material is therefore referred to as M41S. Its average BJH pore diameter is 8.0 nm, the specific BET surface area is 1100 m²/g and the specific pore volume 2.6 cm³/g. A synthesis gel with the molar composition 1 SiO₂: 0.262 Na₂O: 0.109 HTMA-Cl: 0.040 DTMA-Br: 0.72 mesitylene: 31.5 H₂O was used (HTMA/DTMA stand for hexadecyl-/dodecyl-trimethylammonium). The role of the mesitylene is to swell the templating micelle to obtain larger pores than in hexagonally ordered MCM-41. The gel was treated at 373 K for 96 h in a Teflon vessel. After 24, 48 and 72 h of treatment the gel was cooled to ambient temperature and the pH was adjusted by addition of

concentrated acetic acid. The added amounts accounted for SiO₂: CH₃COOH molar ratios of 0.15, 0.07 and 0.04 (total 0.26) after 24, 48 and 72 h, respectively. After 96 h the solid was filtered off, washed with demineralized water and ethanol. The wet M41S material was dried at 323 K in an evacuated oven and calcined during 4 h at 813 K.

Functionalization reactions were performed with (3-aminopropyl)trimethoxysilane (APTMS) and methyltrimethoxysilane (MTMS) as reactive species (Scheme 1). Prior to functionalization the mesoporous M41S material was refluxed in water (25 ml per g of support) for 1 h. After the water treatment the material was collected by filtration and washed with toluene (20 ml/g). The wet material was suspended in toluene (100 ml/g) and the majority of the remaining water was removed during 2 h of azeotropic distillation (~2.5 ml/g). After cooling to ambient temperature pure APTMS (3.6 ml/g), MTMS (2.8 ml/g) or both silanes were added to the slurry. In the latter case MTMS was added before APTMS. The total amount of silane was kept constant at 19 mmol of reactive silane per g of support. Mixtures of APTMS and MTMS are identified by the molar ratio of the silanes in the reaction mixture. For example, 1 g of support with APTMS/MTMS 1:5 was reacted with 0.7 ml (3.2 mmol) APTMS and 2.2 ml (15.8 mmol) MTMS. The mixture was vigorously stirred for 14 h at room temperature. Then the solid was filtered off, redispersed in fresh toluene (100 ml/g) and refluxed for 1 h. The solid was collected by filtration and washed with isopropanol (20 ml/g). In one experiment a Soxhlet extraction was performed at this stage. The functionalized material was placed in a Soxhlet filter and treated with a 2:1 diethyl ether: acetonitrile mixture for 24 h. The functionalized material was dried at 373 K in an evacuated oven.

2.2. Characterization

N₂ physisorption measurements were performed at liquid nitrogen temperature with a Micromeritics TriStar 3000 apparatus. Prior to the measurements the samples were degassed at 673 K and 10 Pa for at least 4 h. The surface area was determined from the adsorption branch of the isotherm according to the BET method in the relative pressure range 0.02 < p/p_0 < 0.2. The total pore volume was calculated from the volume of adsorbed nitrogen at a relative pressure of $p/p_0 = 0.97$. The average BJH pore diameter d was calculated using the formula $d = 4V/A$, where V and A are the cumulative BJH pore volume and the BJH surface area determined from the desorption branch of the isotherm respectively. Organic elementary analysis (CHN) was performed on a LECO CHN-900 apparatus. The organic material in a sample of 2 mg of functionalized M41S was combusted at 1273 K in a flow of He with O₂ and the amounts of

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