

Low-temperature reaction of trialkoxysilanes on silica gel: a mild and controlled method for modifying silica surfaces

E. Péré, H. Cardy, V. Latour, S. Lacombe *

Laboratoire de Chimie Théorique et de Physico-Chimie Moléculaire, UMR CNRS 5624, Université de Pau, B.P. 1155, 64013 Pau Cedex, France

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Abstract

The room temperature reaction of 4-(triethoxysilyl)butyronitrile, 4-TBN ((C₂H₅O)₃-Si-(CH₂)₃-CN), on weakly hydrated silica samples pretreated at 393 K has been studied by desorption experiments and by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy at different aging times under various water partial pressures. The reaction is demonstrated by the decrease of desorption of 4-TBN with time and the simultaneous disappearance of the 2980 and 1394 cm⁻¹ signals in the DRIFT spectra, assigned to the CH₃ moiety of the ethoxy functions. Water partial pressure is shown to have a crucial effect on the rate and efficiency of the process as, after 6 days, for samples kept at room temperature under vacuum, ca. 50% of the silane has reacted, while for those kept in a water-saturated atmosphere the silane reaction reaches 96%. Although the silane appears to be irreversibly bonded to the surface, no definite conclusion may be drawn from these preliminary results as to the nature of the bonding (grafting or coating). These samples are compared to modified silicas prepared according to conventional methods. The same extent of silane reaction (50%) is achieved for preadsorbed samples kept under vacuum and either cured at 473 K for 30 h or kept at room temperature for 6 days. A mild and controlled modification of silica by triethoxysilanes can thus be achieved by first physisorbing known amounts of the modifying silanes from an organic solvent on pretreated silica and then letting the samples mature for a few days at room temperature in a water-saturated atmosphere.

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1. Introduction

Surface-modified silicas are receiving much attention because of their potential use as chromatographic packings [1–5], supported catalysts [6–15], or photocatalysts [16–27], to mention only some of their numerous applications. Treatments with reactive silanes are among the major methods of modification used to convert silicas into materials carrying covalently bonded functional groups [5,28]. Nearly all of these materials are prepared according to a well-known method: the previously dried porous support is heated under reflux for several hours in a toluene or xylene solution of the organic precursor X₃Si–R, commonly a trialkoxysi-

lane or a trichlorosilane derivative of the molecule R to be grafted. After this step, extensive washing or Soxhlet extraction of the modified silica in a variety of solvents is generally performed, in order to eliminate unreacted X₃Si–R or low-molecular-weight soluble molecules arising from hydrolysis and/or polymerization of the silane precursor X₃Si–R.

Some reports describe an alternative grafting method: a known amount of a pretreated silica is soaked for several hours at ambient temperature in a toluene solution of the silane precursor X₃Si–R. After filtration and washing with toluene, the silica gel is cured in an oven between 353 and 473 K [29–33].

Depending on the conditions (water content of the solvents and of silica gel after pretreatment, curing conditions), partial hydrolysis and polymerization of the silane moiety in the solvent or on the surface may also occur, resulting in the formation of siloxane molecules [32,34–37].

* Corresponding author. Fax: +33-559-407-451.

E-mail address: sylvie.lacombe@univ-pau.fr (S. Lacombe).

The temperature at which the pretreatment of the silica is carried out is a crucial point which affects the amount of physisorbed water remaining on the silica surface and the type (isolated, geminal, vicinal) and number of silanol groups [38]. It is known that desorption of physisorbed water is completed around 463 K under vacuum and that at this pretreatment temperature the number of silanol groups is around 4.6 nm^{-2} .

Only a few reports deal with the influence of the curing atmosphere and temperature on the reactivity of trialkoxysilanes towards silica gel [32,39,40].

In connection with our interest in modified silica for photosensitization purposes [25,26], we address in this work the conditions of the room temperature reaction of $X_3\text{Si-R}$ on silica gel in order to prepare organically modified silica gel under mild conditions, avoiding extensive time-consuming washing of the material, and to control the amount of silane actually loaded onto the surface.

We therefore studied the interaction of the model molecule 4-(triethoxysilyl)butyronitrile, 4-TBN ($(\text{C}_2\text{H}_5\text{O})_3\text{-Si-(CH}_2)_3\text{-CN}$) with silica gel. Its behavior on the surface under different atmospheres at room temperature was followed by two complementary methods, namely its desorption at room temperature from the loaded materials and its evolution by analysis of the diffuse reflectance infrared Fourier transform (DRIFT) spectra of the loaded silica gels. Moreover, the DRIFT spectra of these materials were compared to those of samples obtained under conventional grafting methods (curing under vacuum at higher temperature or refluxing toluene). These preliminary results indicate a milder alternative method for the preparation of organically modified silica gels.

2. Experimental part

In order to quantify the loading of the silane derivative on silica gel, a precursor molecule with an easily detectable infrared band was chosen. Commercially available 4-(triethoxysilyl)butyronitrile or 4-TBN ($(\text{C}_2\text{H}_5\text{O})_3\text{-Si-(CH}_2)_3\text{-CN}$) was used as a probe for this purpose. It is characterized by a CN stretching vibration at 2258 cm^{-1} , not overlapping with any band of silica or solvents.

4-(Triethoxysilyl)butyronitrile (4-TBN) and silica gel (Reference 40,360-1: 70–230 mesh, specific area $300 \text{ m}^2 \text{ g}^{-1}$, pore size 100 \AA) were purchased from Aldrich. Silica gel was dried in a vacuum oven at 393 K for 24 h before use. Under these conditions, the desorption of physisorbed water is not complete. The usual weight loss is about 5%. Carbon tetrachloride (spectroscopic grade, Merck), used to prepare the triethoxysilane solutions, was dried over molecular sieves.

For the adsorption isotherm, samples were prepared by adding 0.5 g of dried silica gel to 50 cm^3 of carbon tetrachloride solutions of 4-TBN at different concentrations. The resulting suspension was stirred on an ellipsoidal table for

4 h, as after this time the solution is equilibrated. It was removed by filtration and concentrated under vacuum to 5 cm^3 . Quantitative analysis was performed by transmission FTIR by measuring the area of the 2258 cm^{-1} band corresponding to the CN stretching vibration. The amount of 4-TBN adsorbed on silica is thus deduced from the difference from the initial concentration of the solution.

For the study of the loaded silicas (desorption and DRIFT monitoring), a silica gel sample was prepared by adding about 9 g of dried silica gel to 100 cm^3 of a ca. $10^{-1} \text{ mol l}^{-1}$ solution of 4-TBN in CCl_4 , which corresponds to $1.1 \times 10^{-3} \text{ mol}$ of 4-TBN available in solution per gram of silica. After being stirred on an ellipsoidal table for 4 h, the solution was filtered and the solvent on the loaded silica gel was evacuated at 298 K under vacuum for 24 h. The quantitative determination of the filtrate concentration by FTIR (integration of the CN vibration band) leads to the silica gel loading ($5.28 \times 10^{-4} \text{ mol g}^{-1}$). The loaded silica gel was divided into 36 samples (about 0.25 g each). A first series of 12 samples was kept under reduced pressure ($6 \times 10^{-2} \text{ atm}$) at 298 K (series V). Another 12 samples were kept in a water saturated atmosphere at 298 K (series M) and the last 12 samples were left in the ambient atmosphere (series A). Samples of each series were then analyzed both by desorption and by DRIFT after different periods of time.

For desorption studies, 0.2 g of each sample was stirred in 50 cm^3 of dry CCl_4 at room temperature for 4 h, as preliminary analysis had shown that the solutions were equilibrated after this time. After filtration, each solution was concentrated to 5 cm^3 for accurate determination of the 4-TBN concentration by integration of the CN vibration band of the FTIR transmission spectrum. The repeatability over 10 samples of the same concentration is good, as the relative error is determined to be 3.5%.

For the infrared analysis, the transmission and DRIFT spectra were collected on a Magna 560 Nicolet spectrometer flushed with dried air, with a resolution of 4 cm^{-1} after signal averaging of 200 scans. For transmission studies of solutions, a DTGS detector was used. The DRIFT spectra were recorded with the SPECTRA TECH Inc. collector diffuse reflectance accessory. A wideband liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector was used. In order to ensure good repeatability (relative error 5%) and to obtain quantitative data [41], the samples were diluted in a KBr matrix, previously dried at 373 K, and the mixture was ground before analysis. All the spectra were recorded against that of a pure KBr reference. For each spectrum, it is most important that the sample cup is always adjusted to get the maximum signal indicated by the magnitude of the centerburst of the interferogram. Alternatively, for the curing study at different temperatures of preadsorbed samples, a high-temperature environmental chamber (HTEC from SPECTRA TECH Inc.) was used; this accessory is designed to obtain in situ DRIFT spectra at controlled elevated temperatures and reduced pressure ($6 \times 10^{-2} \text{ atm}$).

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