

Application of ^{13}C and ^{29}Si MAS NMR to the Surface Characterization of a Barbituric Derivative Anchored on Silica

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Abstract: Chemical anchoring of compound layers on silica surfaces are obtained by condensation reactions of silanol groups from silica with alkoxy groups of silyl-terminated coupling agents. The main procedure consists of immobilizing a precursor functional molecule on the support, which is usually carried out with a silylated agent containing a trialkoxysilyl group that reacts with the silanol on the surface. Subsequent reactions can expand the organic covalent chain with desirable functional groups on the solid surface. The purpose of this work is to use solid state NMR to monitor the immobilization on silica of a new linker for primary amines, derived from the condensation of dimethyl barbituric acid and glutaric anhydride, named DGB (Dimethyl-Glutaryl-Barbituric Acid). When this molecule is covalently attached on silica gel, it behaves similarly to DAB (Dimethyl-Acetyl-Barbituric Acid), recently reported as a new protection group for primary amines. The ^{13}C CP/MAS spectrum of the organosilicon compound obtained after reaction on the silica surface with 3-aminopropyltriethoxysilane shows the expected three signals. On the other hand, the ^{29}Si spectrum of the raw silica presented three signals at -91ppm [Q^2 sites $\text{Si}(\text{O}_2)(\text{OH})_2$], -101ppm [Q^3 sites $\text{Si}(\text{O}_3)(\text{OH})$] and also at -110 ppm [Q^4 sites SiO_4]. After the reaction with the 3-aminopropyltriethoxysilane, new signals in the range -45 to -80 ppm due to O-Si-C emerged, confirming the reaction as observed in the ^{13}C NMR spectrum. By comparing the ^{13}C NMR spectra of barbituric derivative samples before and after the coupling reaction with aminopropylsilica, the formation of the amide linkage could be confirmed through the signal at 176 ppm, absent in the ^{13}C spectra of both reagents. It can be concluded that anchoring silanes on the surface of silica was effective thus providing a new route for the synthesis of protecting groups for amines.

Inorganic oxides such as silica gel have received great attention not only due to their surface reactivity, but also to their ability of immobilizing organic molecules on their surface. The interest in these new kinds of materials is reflected in applications such as chemically bonded stationary phases for chromatography, supports for catalysts, and uses in pre-concentration of sorbents, ion exchange or biotechnology.

Chemical anchoring of compound layer on silica surfaces are obtained by condensation reactions of silanol groups from silica with alkoxy groups of silyl-terminated coupling agents.¹ The main procedure consists of immobilizing a precursor functional molecule on the support, which is usually carried out with

a silylated agent containing a trialkoxysilyl group that reacts with the silanol on the surface. Subsequent reactions can expand the organic covalent chain with desirable functional groups on the solid surface.

In a previous work, solid state NMR techniques were applied to characterize polymer anchoring coupling reactions.² The purpose of this work is to use solid state NMR to monitoring the immobilization of a new linker for primary amines on silica, derived from the condensation of dimethyl barbituric acid and glutaric anhydride, named DGB (Dimethyl-Glutaryl-Barbituric Acid). When this molecule is covalently attached to silica gel it behaves similarly to DAB (Dimethyl-Acetyl-Barbituric Acid). DAB was recently reported as a new

protective group for primary amines.³ Silica (Merck, 70-230 Mesh) previously activated was refluxed in dry toluene with 3-

aminotriethoxysilane to give organosilicon 1, which was then reacted with DGB, HOBT and DIC in DMF to give organosilicon 2 (Figure 1).

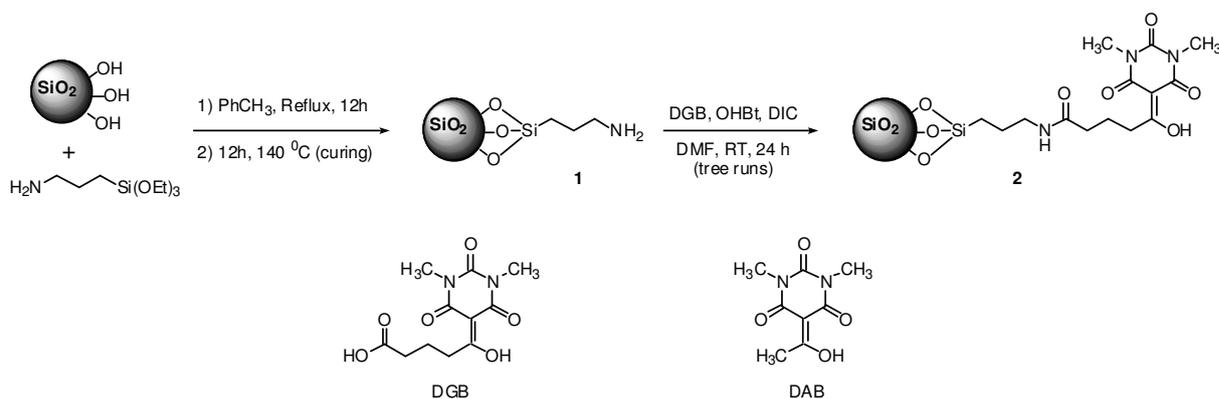


Figure 1. Scheme for the synthesis of products (1) and (2).

Solid state NMR spectra were carried out using a Bruker DRX-300 spectrometer (7.05 t) equipped with a 4mm CP/MAS probe, operating at 75.4MHz (for ¹³C) and 59.3 MHz (for ²⁹Si). Magic angle spinning was performed at 5 kHz spinning rate. The contact time in ¹³C CP/MAS NMR studies were in the range of 1-5 ms; recycle time 5 s and 3200 scans. For ²⁹Si MAS spectra a recycle time of 60s was used and 1000 scans were acquired. Samples of kaolinite (-91.5 ppm) and hexamethylbenzene (CH₃ at 17.3 ppm) were used as references for ²⁹Si and ¹³C spectra resp.

The ¹³C CP/MAS spectrum of the organosilicon obtained after reaction of silica surface with 3-aminopropyltriethoxysilane

(Figure 2) shows three signals at 43 ppm (CH₂-NH₂), 22 ppm (CH₂-CH₂-NH₂) and 10 ppm (Si-CH₂). The signal due to O-CH₂CH₃ (around 68 ppm) of the ethoxy group was not observed, thus indicating that the reaction was complete. On the other hand, the ²⁹Si spectrum of the raw silica presented three signals at -91ppm [Q² sites Si(O₂)(OH)₂], -101ppm [Q³ sites Si(O₃)(OH)] and also at -110 ppm [Q⁴ sites SiO₄].

The reaction with 3-aminopropyltriethoxysilane caused the reduction in the intensities of Q² and Q³ sites. Also, new signals in the range -45 to -80 ppm due to O-Si-C emerged, confirming the reaction as observed in the ¹³C NMR spectrum.

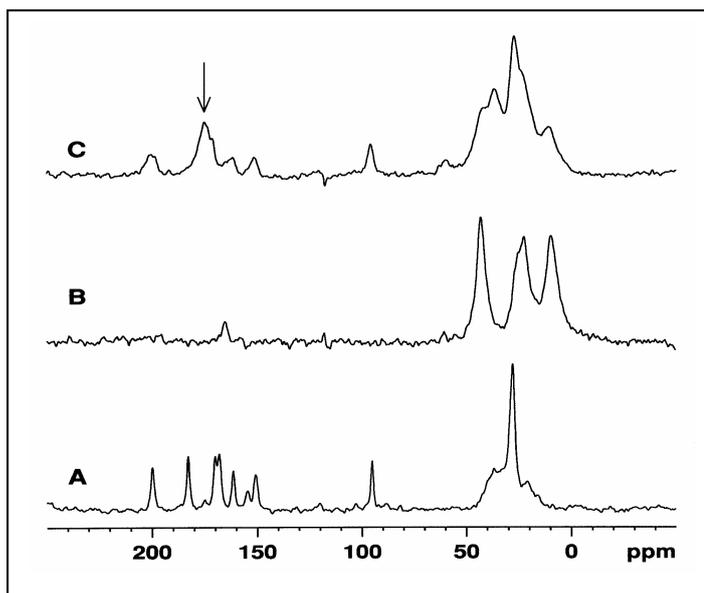


Figure 2. Solid state ^{13}C CP/MAS NMR spectra of DGB (A), organosilicon 1 (B) and organosilicon 2 (C).

By comparing the ^{13}C NMR spectra of barbituric derivative samples before and after the coupling reaction with aminopropylsilica, the formation of the amide linkage could be confirmed through the signal at 176 ppm, absent in the ^{13}C spectra of both reagents.

It can be concluded that anchoring silanes on the surface of silica was effective, thus providing a new route for the synthesis of protecting groups for amines.

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