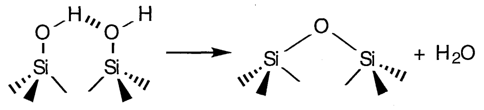
Surface Organometallic Chemistry of Tin: Grafting Reactions on Highly Dehydroxylated Silica

Mariko Adachi, Frédéric Lefebvre, and Jean-Marie Basset*
Laboratoire de Chimie Organométallique de Surface UMR CNRS-CPE 9986,
43, Bd. du 11 Novembre 1918, 69616 Villeurbanne Cédex, France

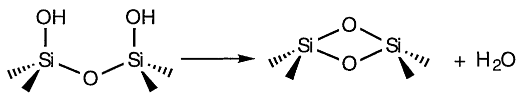
(Received November 20, 1995)

A new grafting method of organotin complexes with the surface of highly dehydroxylated silica is reported. Characterisation was achieved by surface microanalysis, *in situ* IR, solid state ^{13}C CP-MAS and ^{119}Sn MAS NMR. Bu_3Sn-O-$SnBu_3$ reacts with the strained siloxanes and opens these bridges at room temperature. The reaction occurs also with the remaining hydroxyl groups and with less strained siloxane bridges, leading in all cases to the same surface organometallic fragment ≡Si-O-$SnBu_3$.

In most cases, organometallic complexes are grafted on oxide surfaces via specific reactions using hydroxyl groups which can react as nucleophiles or as electrophiles[1]. However it seems possible to use another approach for the grafting of organometallic complexes which consists in reacting them with ≡Si-O-Si≡ bonds. It is well known that thermal treatment of silica at temperatures between 200 and 500 °C results in a condensation of adjacent silanol groups according to:

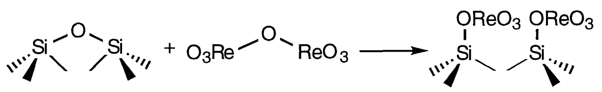


Depending on the location of the silanols on the silica surface and the dehydroxylation process, this induces the formation of cycles with 3, 4 or more silicon atoms. Highly strained siloxane bonds are thus readily formed on high surface area silica samples dehydrated at temperatures above ca. 600 °C.[2] These highly reactive sites are formed by reaction of two adjacent isolated silanol groups.



On silica dehydroxylated at 1100 °C, the maximum number of these sites has been estimated to be about 0.15 nm^{-2} [3] while the density of residual hydroxyl groups is approximately 0.4 nm^{-2}.[4]

We have recently reported that reaction of Re_2O_7 (or Me_3Si-O-ReO_3) with these highly strained siloxane bridges of silica results in the cleavage of the Si-O-Si bridge.[5]



We believed that Bu_3Sn-O-$SnBu_3$ should react similarly with silica that is via the opening of the highly strained siloxane bridges. In order to check this hypothesis, a disk of silica (Aerosil 200, Degussa, m = 10 mg) was introduced in an infrared cell for *in-situ* measurements. This cell was equipped with ZnSe windows and with a quartz tube allowing heating up to 1000 °C. The silica sample was first treated under vacuum (10^{-4} torr) at room temperature. It was then calcined at 500 °C for 3 h under flowing oxygen. Finally, it was dehydroxylated under vacuum at 1000 °C for 14 h (silica$_{(1000)}$). After cooling at room temperature a drop of Bu_3Sn-O-$SnBu_3$ (Aldrich, > 99% purity) was introduced onto the silica disk. Infrared spectra were then recorded at various intervals of time.

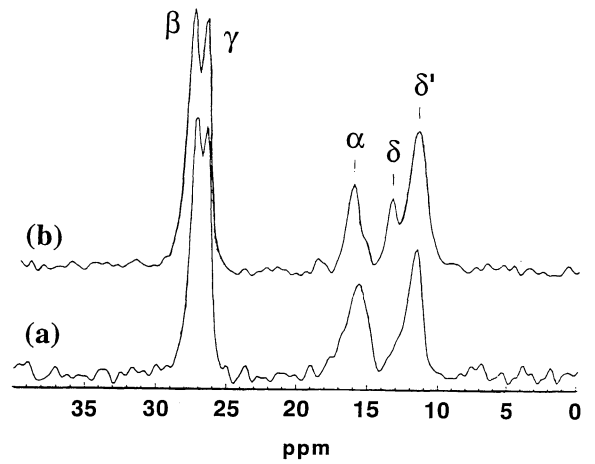


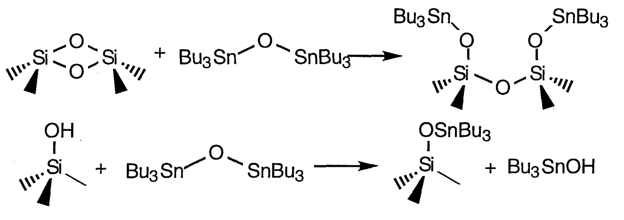
Figure 1. ^{13}C CP-MAS NMR spectra of grafted tributyltin on (a) silica$_{(1000)}$ (b) silica$_{(200)}$ (non washed samples).

The infrared spectrum of the silica$_{(1000)}$ showed a sharp band of very small intensity at 3747 cm^{-1} corresponding to the few isolated silanol groups remaining on the surface. Two relatively broad bands were also observed at 909 and 889 cm^{-1}, previously attributed to ν(Si-O) vibrations of the highly strained siloxane bridges.[5]

Some minutes after introduction of Bu_3Sn-O-$SnBu_3$, the bands at 3747, 909 and 889 cm^{-1} had completely disappeared, probing that the few remaining silanol groups as well as the strained siloxane bridges had reacted. After washing with *n*-pentane in order to remove unreacted Bu_3Sn-O-$SnBu_3$, elemental analysis gave a ratio C/Sn of 12.0 corresponding to 3 butyl groups per tin atom.

The ^{13}C and ^{119}Sn solid state NMR spectra of a sample prepared using the same procedure were quite similar to those previously reported for the ≡Si-O-$SnBu_3$ obtained by reaction of $SnBu_4$ or $HSnBu_3$ with a silica$_{(200\ \mathrm{or}\ 500)}$.[6] The ^{119}Sn MAS NMR spectrum showed a broad peak at ca. 100 ppm vs. $SnMe_4$ while the ^{13}C CP-MAS NMR spectrum showed peaks at 11.7, 15.7, 26.6 and 27.3 ppm respectively attributed to C_δ, C_α, C_γ and C_β carbon atoms of the butyl ligands of the grafted ≡Si-O-$SnBu_3$ species (Figure 1).

We can then reasonably propose that both hydroxyl groups (minor amount) and highly strained siloxane bridges of silica activated at 1000 °C (major amount) react with Bu_3Sn-O-$SnBu_3$ leading to the formation of the well defined grafted species ≡Si-O-$SnBu_3$. Such reactions may be written as follows:



The reaction of Bu_3Sn-O-$SnBu_3$ with the highly strained ≡Si-O-Si≡ bridges is quite similar to that reported for ReO_3-O-ReO_3 or with alkylalkoxysilanes ($R'_nSi(OR)_{4-n}$, R' = H, Me, Et; n = 1~3).[7] However, in order to have further evidence of the reaction of the hydroxyl groups, we studied the reaction of Bu_3Sn-O-$SnBu_3$ with a silica dehydroxylated at a lower temperature, namely 200 °C. The reaction occurs at room temperature, leading also to the formation of ≡Si-O-$SnBu_3$ as evidenced by ^{13}C and ^{119}Sn solid state NMR. The main differences of the ^{13}C CP-MAS NMR spectrum with that recorded after reaction with $silica_{(1000)}$ are: (i) the C_α peak is broader, showing the greater diversity of anchorage sites on $silica_{(200)}$ compared to $silica_{(1000)}$ and (ii) the appearance of a new C_δ peak at 13.4 ppm corresponding to chains which are not interacting with the surface via van der Waals interactions. This can be explained by the lower tin loading on $silica_{(1000)}$ compared to $silica_{(200)}$.

It can now be interesting to discuss the highest tin loading which can be achieved on $silica_{(1000)}$. After washing by pentane tin loading was found to be 4.69 wt%. Considering that, on $silica_{(1000)}$ there are 0.15 highly strained siloxane bridges and 0.4 hydroxyl groups per nm^2, this should correspond to a tin loading of only 1.18 and 1.58 wt% respectively, that is a 2.76% total. It is then necessary to suppose that less strained siloxane bridges can also react. This is probably related to the formation of Bu_3Sn-OH which should be more reactive than Bu_3Sn-O-$SnBu_3$.

We studied also the reaction of Bu_3Sn-S-$SnBu_3$ [8] with $silica_{(1000)}$. Quite similar results were obtained, especially the ^{13}C CP-MAS and ^{119}Sn MAS NMR spectra were identical to those of ≡Si-O-$SnBu_3$. The main difference was the chemical analysis of the samples after washing: Indeed the tin loading was found to be 2.23 wt%, while the sulfur content was ca. 0.1 wt%. This can be easily explained if one assumes that only the strained siloxanes and the hydroxyl groups reacted (theoretical amounts: Sn = 2.76 wt%; S = 0.16 wt%). Bu_3SnSH formed by reaction of the hydroxyl groups should then be inactive versus the less strained siloxane bridges.

In conclusion, it has been shown that Bu_3Sn-O-$SnBu_3$ reacts not only with the highly strained siloxane bridges of $silica_{(1000)}$ but also with the less strained siloxane bridges and with the remaining hydroxyl groups. This reaction occurs at room temperature and very rapidly. This method allows the synthesis of neighboring ≡Si-O-SnR_3 fragments. This can be readily applied to the modification of the pore entrance of highly siliceous zeolites, known to have a very high thermal stability and should result in a modification of their adsorption properties, by varying the size of the R fragments.

References

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