

Versatility of silica used as a ligand: effect of thermal treatments of silica on the nature of silica-supported alkyl tantalum species

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

Abstract

The tris(neopentyl)neopentylidene tantalum complex reacts with the silanol groups of silica dehydroxylated at temperatures ranging from 300 to 700°C to form well-defined surface organometallic species. For a silica dehydroxylated at 300°C, the amount of available silanols allows the formation of species **3** linked by two covalent bonds to silica, while the dehydroxylation at 700°C leads to the formation of species **2** with only one covalent bond to silica. Dehydroxylation thus constitutes a way to control the hapticity of silica towards organometallic complexes. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Changing the properties of an organometallic complex can often be obtained via modification of its ligands. Taking advantage of this, inorganic chemists have been able to design catalysts specifically tuned for a desired reaction [1]. In this article, we want to show that such a concept can be extended to the case of surface organometallic chemistry [2], although the main ligand, an inorganic surface, does not exhibit the usual versatility of the commonly used organic ligands.

It has been shown that the reaction of **1**, $\text{Ta}(\text{=CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$, with silica dehydroxylated at 500°C ($\text{SiO}_{2-(500)}$) leads to the formation of two surface species: $(\text{=SiO})\text{-Ta}(\text{=CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_2$ (**2**) and $(\text{=SiO})_2\text{Ta}(\text{=CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)$ (**3**) in a ratio close to 1:1 [3]. The grafting of the organometallic fragment occurs via a reaction with the silanol groups of the silica surface [4]. Here, we investigate how changes in the nature and the overall concentration of the surface =SiOH groups can

affect the nature of the resulting surface species. A simple way to modify the surface of silica consists in heating it for several hours under vacuum. In this study, three thermal treatments at different temperatures (300, 500 and 700°C) have been used and their effects on the further reaction with **1** have been investigated [5].

2. Experimental

All experiments were conducted under strict inert atmosphere or vacuum conditions using break-and-seal and Schlenk techniques. Infrared spectra were recorded on a Nicolet Magna 550-FT spectrometer equipped with a cell designed for in situ preparation under controlled atmosphere [6]. Gas phase analyses were performed on a gas chromatograph HP 5890 equipped with a flame ionization detector and a $\text{Al}_2\text{O}_3/\text{KCl}$ on fused silica column (50 m × 0.32 mm). Elemental analyses were performed by the CNRS Central Analysis Service of Solaize. Silica was purchased from Degussa (non-porous, Aerosil, 200 $\text{m}^2 \text{g}^{-1}$). The complex **1**, $\text{Ta}(\text{=CHC}(\text{CH}_3)_3)(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$, was prepared accord-

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ing to the literature procedure [7]. Pentane and ether were distilled under N_2 from sodium benzophenone ketyl solutions. Perdeuterated ethanol purchased from SDS was degassed by three freeze-pump-thaw cycles. The H_2 was dried over freshly regenerated molecular sieve (3 Å) and deoxo traps just before addition.

The surface complexes were prepared following two different procedures [8].

1. Reaction of **1** via sublimation with silica treated at different temperatures. Silica (20–40 mg) was pressed into an 17-mm self-supporting disk, put into a sealed glass high-vacuum reactor equipped with CaF_2 windows, and dehydroxylated under vacuum at various temperatures: (a) 300°C (15 h), (b) 500°C (15 h), or (c) 500°C (15 h) followed by 700°C (4 h) [9]. The compound **1** was then sublimed at 75°C on the silica disk, which turned orange. After 1 h of reaction at 75°C, the excess of **1** was removed by reverse sublimation in a liquid nitrogen cooled tube, which was then sealed off using a torch. The tantalum surface complexes thus synthesized were then further characterized by microanalysis, IR spectroscopy and reactions with ethanol and hydrogen.
2. Reaction of **1** via impregnation with silica treated at various temperature. A suspension of silica (1 g), previously dehydroxylated at the desired temperature as previously described above, in pentane (15 ml) was treated at 25°C with a solution of **1** (0.155 g, 0.33 mmol) in pentane under an inert atmosphere. The reaction mixture was stirred for 2 h at 25°C and filtered. The remaining orange solid was then washed three times with pentane and dried under vacuo. The tantalum surface complexes were further characterized by microanalysis and reactions with ethanol and hydrogen.

2.1. Reaction of the surface tantalum complexes with perdeuterated ethanol

The silica supported tantalum species was treated with perdeuterated ethanol at 150°C for 15h, and the reaction was followed by IR spectroscopy. After complete reaction of the neopentyl ligands of the surface complex, the amount of neopentane was measured by GC.

2.2. Reaction of the surface complexes with H_2

The silica supported tantalum species was treated with dry H_2 (500–700 equiv.) for 15 h at 150°C, and the reaction was followed by IR spectroscopy. The amounts of methane (resulting from the total hydrogenolysis of surface neopentyl groups) were measured by GC.

3. Results and discussion

Numerous studies [10] on non-porous silica have shown that two main functional groups are present on the surface: siloxane ($\equiv Si-O-Si \equiv$) and silanol ($\equiv Si-O-H$) groups. Silanols have been classified into three types, depending on the nature of their environment: geminal (for two OH groups on the same Si atom), vicinal (for OH groups on different Si atoms, but interacting via H-bonds), and isolated. While the existence of geminal silanols is still a matter of debates, vicinal and isolated silanols have been identified by NMR and IR spectroscopies [10b]. A thermal treatment of the silica surface leads to the condensation of the hydroxyl groups to form siloxane bridges. This process, called dehydroxyla-

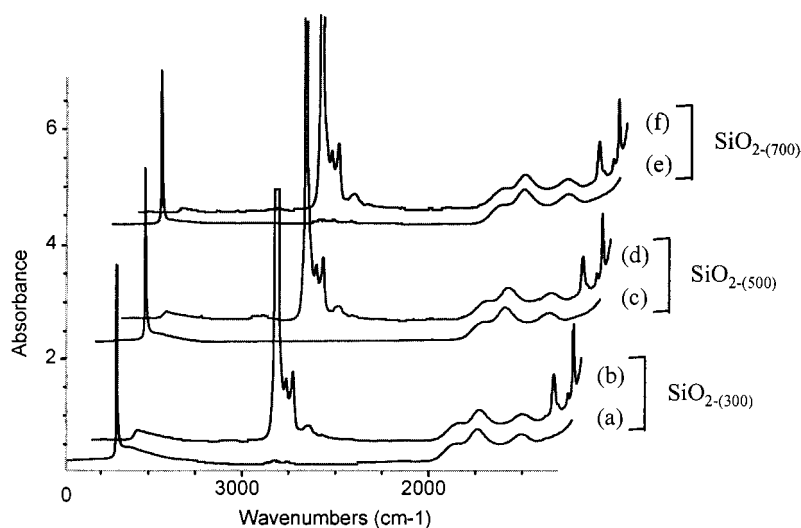
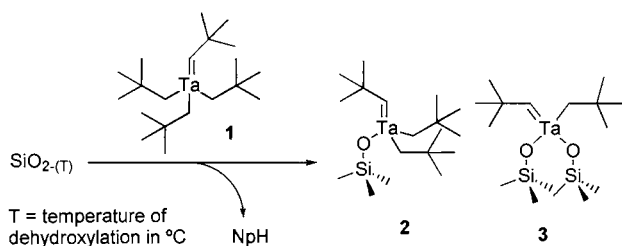


Fig. 1. IR spectra of (a) SiO₂₋₍₃₀₀₎; (b) SiO₂₋₍₃₀₀₎ after reaction with **1**; (c) SiO₂₋₍₅₀₀₎; (d) SiO₂₋₍₅₀₀₎ after reaction with **1**; (e) SiO₂₋₍₇₀₀₎; (f) SiO₂₋₍₇₀₀₎ after reaction with **1**.



Scheme 1.

tion, first implies vicinal silanols at the temperature range 200–400°C and then isolated silanols above 400°C. Overall, the dehydroxylation leads to the decrease of the surface hydroxyl concentration. Fig. 1(a, c, e) shows the IR spectra obtained for an aerosil silica (Degussa, 200 m² g⁻¹) dehydroxylated at 300, 500 and 700°C. The intensities of both the sharp band (3747 cm⁻¹, isolated silanols) and the broad band (3500–3750 cm⁻¹, interacting silanols) decrease with the temperature of treatment. At 700°C, there is only one sharp symmetrical band at 3747 cm⁻¹, corresponding to isolated silanols. These spectra show that the amount of surface hydroxyl groups approximately drops by 50% each time the temperature of treatment was increased by 200°C.

The reaction between a silica surface dehydroxylated at 500°C with **1** has already been studied [3]. It leads to the formation of two surface species **2** and **3** in a ratio close to 1:1 along with the formation of neopentane (Scheme 1).

For silica treated at 300 and 700°C, a similar reaction was observed. Indeed, the sublimation of an excess of **1** on SiO₂₋₍₃₀₀₎ and SiO₂₋₍₇₀₀₎ led to a rapid and complete disappearance of the sharp band (3747 cm⁻¹) of the silanol groups in the IR spectra. For SiO₂₋₍₃₀₀₎ and SiO₂₋₍₅₀₀₎, the broad silanol band (3500–3750 cm⁻¹) is partially consumed [11]. Removing the excess of **1** did not restore the ≡SiOH bands, which confirms that the silanol groups had been irreversibly consumed (Fig. 1(b, d, f)).

The appearance of IR bands around 3000–2800 and 1500–1300 cm⁻¹ can be observed. They do not disap-

pear after desorption of the excess of **1** and evacuation of the gas phase, and can be consequently attributed to the ν(C–H) and δ(C–H) vibrations of the residual alkyl or alkylidene groups of the surface tantalum complexes. The silica pretreatment does not significantly change the observed patterns of these C–H vibration bands.

Elemental analysis was performed on each sample (Table 1, entry 1). Surprisingly, the tantalum content stays roughly the same for each type of silica, although they exhibit very different number of available silanols (vide infra). This would suggest that the amount of the organometallic species grafted is more limited by steric hindrances than by any lack of available ≡SiOH groups. However, the amount of neopentane released in the gas phase during grafting depends on the thermal treatment applied to silica (Table 1, entry 2). This quantity decreases with the increase of the temperature of dehydroxylation, i.e. the number of available ≡SiOH groups on the surface. Since the Ta content stays approximately constant for each type of silica, the ratio of neopentane released per tantalum decreases with the increase of the temperature of the thermal treatment. For SiO₂₋₍₇₀₀₎, around 1 mole of neopentane per mole of tantalum is produced during grafting, leaving an average of three neopentyl groups still bound to the metal center of the surface species. This suggests that the monografted complex **2** is the main product on the surface. On the other hand, the di-grafted complex **3** seems to be the major product formed on SiO₂₋₍₃₀₀₎ since 2 mol of neopentane per tantalum are produced during grafting. An intermediary behavior was obtained on SiO₂₋₍₅₀₀₎, where both mono- and di-grafted species are present in similar quantities.

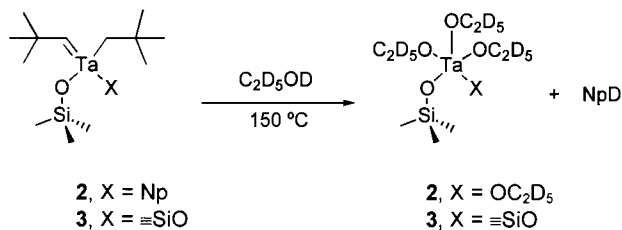
To confirm these first results, reactions with deuterated-ethanol and H₂ were carried out. Alkyl ligands of surface tantalum complexes are completely removed by reaction with ethanol to form ethoxy tantalum surface species with a concomitant evolution of neopentane (Scheme 2) [12].

The reaction was followed by IR spectroscopy using deuterated ethanol to avoid overlaps between C–H vibration bands of neopentyls and alkoxides surface

Table 1
Elemental analysis and amount of gases liberated during the grafting of **1** on the different silica and during the reaction of the surface species with ethanol and H₂

Entry	(1) ^a	(2)	(3)	(4)	(5)
T(°C) SiO ₂	Elem. Anal. Ta (% w)	NpH/Ta (grafting)	NpH/Ta (alcoholysis)	Elem. Anal. ratio (C ₂ H ₅ OH/Ta)	NpH/Ta (hydrogenolysis)
300	6.1	1.7	1.95	3.0	2.25
500	5.5	1.5	2.55	3.55	2.5
700	6.4	1.0	2.9	3.9	3

^a Average value for Ta content obtained for several experiments, which typically varies between 5 and 7%.



Scheme 2.

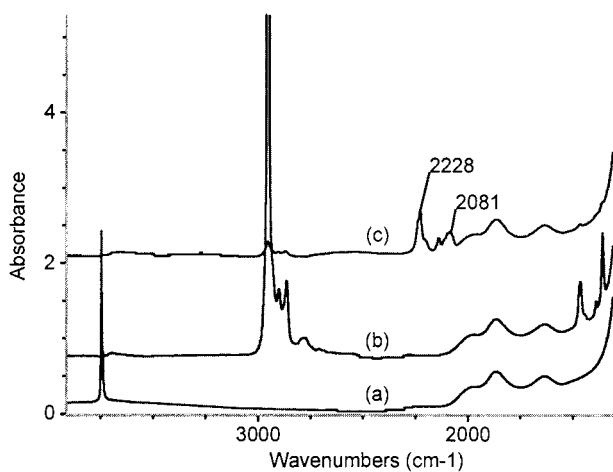
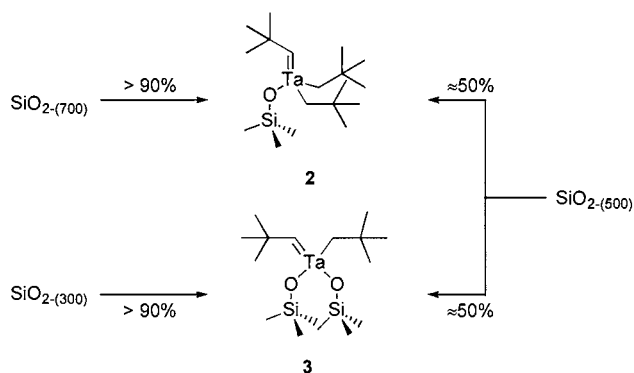


Fig. 2. IR spectra of (a) SiO₂ (700°C); (b) after reaction with **1**; (c) after reaction with C₂D₅OD.



Scheme 3.

groups. IR spectra of the surface species on SiO₂₋₍₇₀₀₎ are shown on Fig. 2 and represent the surface complex: (b) before and (c) after reaction with deuterated ethanol and evacuation of the excess alcohol under vacuum. In spectrum (c), the absence of vibration bands in the 2800–3000 cm⁻¹ region indicates that all the neopentyl and neopentylidene fragments have been released from the metal center. The formation of the ethoxy ligands is confirmed by the appearance of vibration bands in the 2000–2250 cm⁻¹ region corresponding to the ν(C–D) vibrations. Identical results were obtained for SiO₂₋₍₃₀₀₎ and SiO₂₋₍₅₀₀₎. The amount of neopentane liberated in the gas phase was also measured (Table 1, entry 3).

This corresponds to an average of approximately 2 and 3 mol of neopentane per mol of tantalum for SiO₂₋₍₃₀₀₎ and SiO₂₋₍₇₀₀₎, respectively. Again SiO₂₋₍₅₀₀₎ exhibits an intermediary behavior with 2.5 moles of neopentane per mole of tantalum. The mass balance is respected in all cases since four neopentanes (3.65–4.05) per tantalum were produced for the whole process of grafting and alcoholysis starting from **1**, which contains three neopentyl plus one neopentylidene groups (four potential NpH via ethanolysis). Moreover, elemental analyses of the ethoxy tantalum surface species (**2'** and **3'**) are in agreement with these data (Table 1, entry 4). Indeed, it shows that the alkoxy tantalum species prepared on SiO₂₋₍₃₀₀₎, SiO₂₋₍₅₀₀₎ and SiO₂₋₍₇₀₀₎ are bearing on average 3, 3.5, and 3.9 ethoxy ligands, respectively.

Neopentyl and neopentylidene ligands of **2** and **3** can also be completely removed from the metal center by treatment under hydrogen at 150°C leading to a unique surface tantalum hydride species [13]. Only methane, resulting from the total hydrogenolysis of the neopentyl and neopentylidene fragments, is detected in the gas phase. The amounts of methane expressed in neopentane per tantalum (Table 1, entry 5) are in agreement with the results obtained via alcoholysis, thus confirming the nature of the surface species: i.e. grafting on SiO₂₋₍₃₀₀₎ mainly yields the tantalum surface complex **3** linked by 2 siloxy ligands, while the use of SiO₂₋₍₇₀₀₎ favors the tantalum complex **2** anchored with only one siloxy group to the surface.

The tris(neopentyl)neopentylidene tantalum complex **1** has an estimated projected area of 0.9 nm² [14]. On SiO₂₋₍₇₀₀₎, the number of ≡Si–OH per nm² is about 1. Consequently, on average, only one ≡Si–OH can be present in the area covered by an adsorbed organometallic species, which is consistent with the formation of **2** as the major surface complex on SiO₂₋₍₇₀₀₎. Since the content of Ta is typically 6% (in weight) (that is 330 μmol of Ta per g of SiO₂), the total surface occupied by the organometallic fragment is around 180 m² g⁻¹, i.e. 90% of the available area of the silica (200 m² g⁻¹). This shows that the SiO₂₋₍₇₀₀₎ surface is almost completely covered. On SiO₂₋₍₃₀₀₎, the density of ≡Si–OH groups is greater, hence two ≡SiOH should be (or can rearrange to be) close enough to react with the same metal center. This explains the formation of **3** as the major surface complex on SiO₂₋₍₃₀₀₎. The neopentyl-neopentylidene fragment Ta(=CHC(CH₃)₃)(CH₂C(CH₃)₃) has an estimated area of 0.6 nm², which corresponds to a 60% coverage of the silica surface. This low coverage can be due to either the total consumption of all reactive silanols or the steric hindrances of the surface fragments that prevent further reaction with an incoming **1** [15]. Overall, this study has allowed the fairly selective preparation of both **2** and **3** depending on the temperature of treatment of silica (Scheme 3).

4. Conclusion

Control of the mode of grafting of an organometallic species on SiO₂ can be achieved by careful choice of the initial thermal treatment applied to the surface. We have shown that, on average, the silica behaves either as a bidentate or a monodentate ligand depending on its thermal treatment. Far from being as easy to handle as the usual organic ligand, silica, as a ligand has proved to exhibit some versatility, that could be useful in the design of specific catalysts prepared by surface organometallic chemistry.

Acknowledgements

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