

Grafting Reaction of Organotin Complexes on Silica Catalyzed by Tungstic Heteropolyacids

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The grafting reaction of tetramethyltin on silica is catalyzed by $H_4SiW_{12}O_{40}$ preliminary impregnated on the support. While the reaction proceeds at temperatures higher than 150 °C on silica alone, the presence of the polyacid allows the grafting at room temperature. A study as a function of the polyacid coverage has shown that there is a direct correlation between the reaction rate and the number of highly acidic sites on the support, probing that there is a reaction of the tetraalkyltin with them (limiting step) followed by a migration of the grafted fragment on the silica surface. Not only monografted species (as observed on silica) but also multigrafted tin species are formed because of further reactions of the grafted fragments.

Introduction

Tetraalkyl tin reacts with Aerosil silica dehydroxylated at high temperature (200 to 700 °C) to yield monografted $\equiv Si-O-SnR_3$ species which were characterized by various physicochemical methods.¹ The reaction proceeds only at high temperature (150 °C or higher). The same reaction occurs on mesoporous silica (MCM-41 or MS) with only a small difference: when the support has been dehydroxylated at low temperature the formation of multigrafted species ($\equiv Si-O$)_nSnR_{4-n} ($n = 2, 3$) is also observed.² This reaction of tetraalkyl tin with surface hydroxyl groups has been extended to other supports such as cloverite^{3,4} and faujasite HY.⁵ In all cases the same surface organometallic species were formed but the reaction occurred at completely different temperatures than on silica: slowly at room temperature on cloverite and rapidly even at -100 °C on faujasite. This result was explained by assuming that the limiting step of the reaction was the attack of the Sn-C bond by the acidic proton. So, a stronger acid site should lead to a higher reaction rate, and a correlation could be made between these two parameters.

We decided then to use the grafting reaction of tetramethyl tin as a measure of the surface acidity of solid catalysts. We choose first to study this way the acidity of supported

heteropolyacids. Indeed, tungstic heteropolyacids with the Keggin structure are known to be highly acidic and are used in a variety of reactions where they can replace strong liquid acids such as sulfuric acid.⁶ We have recently shown that they react, in their anhydrous form, at room temperature with tetramethyl tin, yielding a trimethyl tin salt of the polyoxometalate.⁷ Supporting these tungstic heteropolyacids on silica results, as evidenced for example by solid-state ¹H MAS NMR,⁸ in a decrease of the number of these strong acid sites. However, depending on the preparation method, the polyacids are more or less dispersed on the support, resulting in variable amounts of these acid sites. It is then important to have methods allowing the determination of their quantity as this will govern the catalytic properties of the solids. As hydroxyl groups of silica react only at high temperature (> 150 °C), it should be possible to determine, by reaction with tetramethyltin at room temperature, the exact amount of strong acid sites on the catalyst.

Results and Discussion

Kinetic Study of the Reaction of the Supported Heteropolyacids with Tetramethyl Tin. As soon as tetramethyltin is contacted at room temperature with $H_4SiW_{12}O_{40}$ supported on silica, methane evolves (Figure 1), in agreement with the expected reaction of tetramethyltin with the strong Brønsted acid sites of the heteropolyacid. However, two behaviors are observed: (i) the kinetic curve

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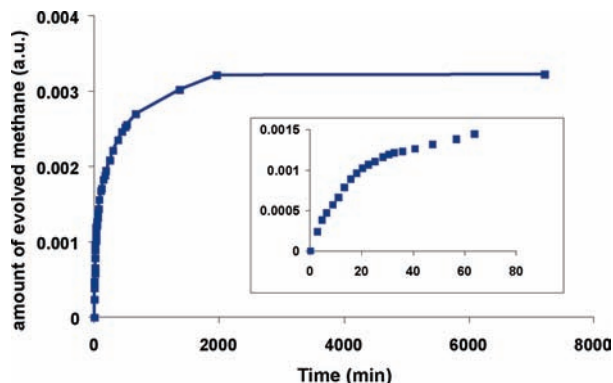
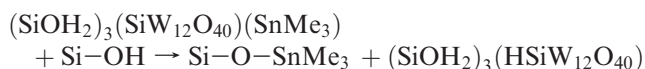
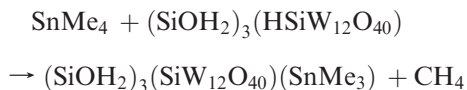


Figure 1. Methane evolution as a function of time during the reaction at room temperature of SnMe_4 with 37.5 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ dehydroxylated under vacuum at 200 °C.

(Figure 1) seems to show two components, a first rapid increase of the methane evolution followed by a slower increase, and (ii) the amount of evolved methane is higher than expected (ca. 16 moles of methane per polyoxometalate). Indeed, we had previously shown that the polyacid is linked to the silica by mainly three bonds (via protonation of the silanol groups) and so only one strong acid site remains.⁸ However the amount of evolved methane after 150 h at room temperature corresponds to more than the total strong acid sites of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. Another feature (Figure 2) can be seen when recording the infrared spectra of the reaction mixture as a function of time. Clearly the silanol groups at 3747 cm^{-1} are affected by the reaction as the IR band decreases with time (the same observation can also be made for the H-bonded hydroxyl groups (broadband between 3700 and 3000 cm^{-1}). Simultaneously new bands appear at 2989 and 2922 ($\nu(\text{C}-\text{H})$), 1715 (?) and 1402 ($\delta(\text{C}-\text{H})$) cm^{-1} . The intensity of these four bands varies similarly as a function of time (a linear correlation can be made between the intensities) and so the band at 1715 cm^{-1} for which we have no attribution at the moment can be correlated to the three other bands.

Clearly, these two observations can lead to only one conclusion: as the amount of evolved methane is higher than the expected value and as the silanol groups disappear, one must conclude that tetramethyltin has reacted with the hydroxyl groups of silica. As on pure silica the reaction proceeds only at high temperature; it is then necessary to suppose that the supported heteropolyacid played the role of catalyst for this reaction, tetramethyltin reacting first with it and then a migration on the support occurs, restoring the acidic proton:



These two equations can also explain the presence of two different rates on the kinetic curve: the first part is probably due to the rapid reaction with the acidic groups of the heteropolyacid while the slower slope corresponds

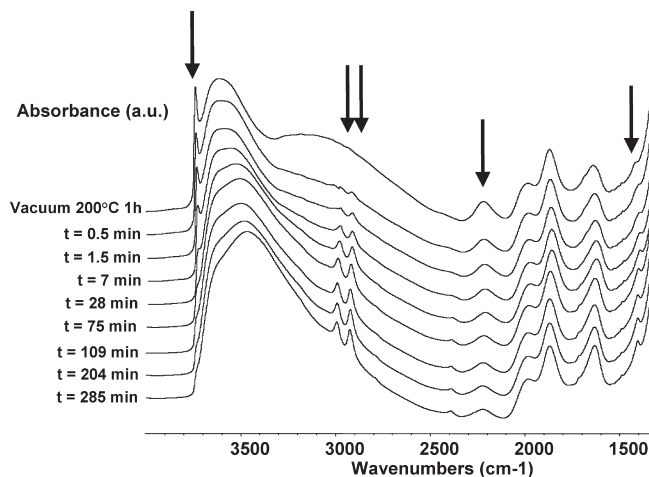


Figure 2. Infrared spectra of 37.5 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ after treatment under vacuum at 200 °C and further addition of SnMe_4 at room temperature.

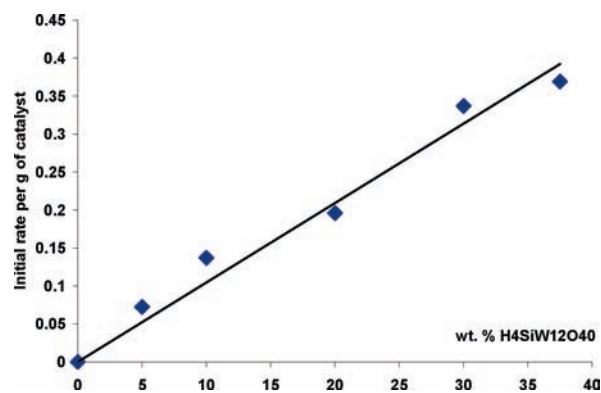


Figure 3. Initial rate of methane evolution as a function of the $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ loading during the reaction of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ with SnMe_4 at 20 °C.

to the diffusion on the support. If these assumptions are true, the reaction rate of methane evolution should be dependent on the amount of silicotungstic acid on the support. We have then undertaken a study of the grafting reaction of tetramethyl tin on $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ catalysts with various polyoxometalate loadings (between 5 and 37 wt %). In each case the initial reaction rate, which should correspond to the first equation above, has been determined and plotted as a function of the polyoxometalate loading (Figure 3). Clearly there is a linear correlation between the methane evolution and the amount of polyoxometalate on the silica, in agreement with a first-order kinetic law and with the above mechanism. In contrast, the amount of evolved methane after a long time is of the same order of magnitude whatever the polyoxometalate loading, showing that it does not depend on it, also in agreement with the above mechanism.

Another proof of the above mechanism can be obtained by using, instead of dodecatungstosilicic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, dodecatungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$, for which we had shown by ^1H MAS NMR that there was no strong acidity remaining after deposition on silica.⁸ In that case the reaction rate is very low (for a 37 wt % loading the curve is quite the same as that obtained with 5 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) showing that tetramethyltin reacts with the strong acid sites of the polyacid.

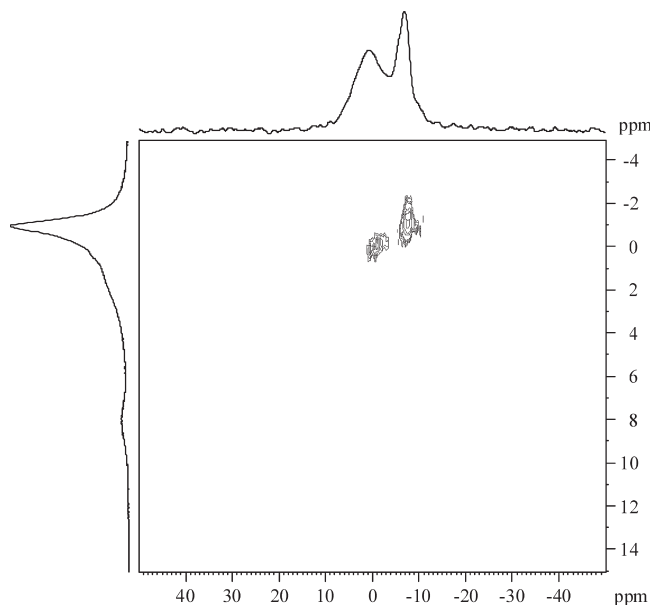


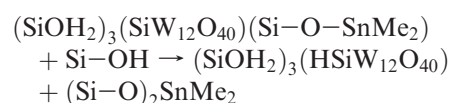
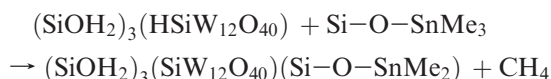
Figure 4. 2D ^1H - ^{13}C HETCOR MAS NMR spectrum of the solid resulting of the reaction of ^{13}C -enriched SnMe_4 with 37.5 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$.

Structure of the Grafted Tin Fragment. The grafted tin fragment was characterized by infrared spectroscopy, ^1H , ^{13}C CP-MAS and ^{119}Sn MAS NMR and by EXAFS. As described above, the infrared spectrum of the grafted tin fragment shows four bands (in the $1300\text{--}4000\text{ cm}^{-1}$ range) at 2989, 2922, 1715, and 1402 cm^{-1} . Three of these bands are characteristic of tin methyl groups, only the band at 1715 cm^{-1} cannot be attributed to the tin-methyl group. The ^1H MAS NMR spectrum after reaction during 150 h shows three components at about 8 ppm (broad), 2.0 ppm (a small shoulder), and an intense peak at about -1 ppm . The first peak corresponds to the acidic proton of the supported heteropolyacid,^{8,9} the second one to some remaining silanol groups, and the last one to tin-methyl fragments. More interestingly, the ^{13}C CP-MAS NMR spectrum does not show only one peak at -7 ppm as expected for the $\equiv\text{Si-O-SnMe}_3$ fragment on silica¹ but also another signal at about 0 ppm, which had been observed upon thermal treatment of the above species and attributed to the doubly silica-bonded complex $(\equiv\text{Si-O})_2\text{SnMe}_2$.¹⁰ 2D ^1H - ^{13}C HETCOR NMR spectra were recorded on the solid after reaction with ^{13}C enriched tetramethyl tin. Two spectra were recorded, one with a short contact time ($200\text{ }\mu\text{s}$) depicted in Figure 4, allowing to observe correlations between H and C atoms directly bonded and one with a large contact time allowing the observation of correlations at higher distances. The spectrum recorded at a short contact time shows only two correlation peaks, one for each ^{13}C signal: the signal at about -7 ppm shows a correlation with a proton at -1.1 ppm while that at about 0 ppm shows a correlation with a proton signal at about 0 ppm, proving the existence of at least two different tin species on the solid. The spectrum recorded at a high contact time does not show

any correlation between these two species and presents only a weak correlation with the acidic proton at about 8 ppm, in agreement with the presence of this proton near some grafted tin fragments.

It could be proposed that the ^{13}C signal near 0 ppm is due to physisorbed tetramethyl tin but this hypothesis can be ruled out because of the following observations: (i) physisorbed species give very sharp signals because of their mobility on the surface, in contrast to what is observed here; (ii) these species are not detected when using cross-polarization or only with a very low sensitivity because of the very bad polarization transfer occurring when the C-H vector is mobile; (iii) and finally the ^{119}Sn MAS NMR spectrum shows only a broad signal at $+130\text{ ppm}$, in agreement with a $\equiv\text{Si-O-SnMe}_3$ species¹ with no peak at 0 ppm characteristic of SnMe_4 . However, the ^{119}Sn MAS NMR signal of the digrafted species was not observed, as on Aerosil silica.¹⁶ This is due to its very large chemical shift anisotropy, as shown by recording the ^{119}Sn MAS NMR spectrum of the corresponding model compound where silica was mimicked by a silsesquioxane molecule.¹¹

So, solid state NMR shows the presence of not only monografted species but also of digrafted species. As a consequence, the above equations are not sufficient, and equations corresponding to a reaction of the trimethyl tin fragment with the acidic proton must be added to them. Our data cannot discriminate between a reaction of the trimethyl tin fragment before or after its migration on silica. To be more general, the two possibilities are included in the following equations:



Chemical analyses are also in agreement with the formation of a mixture of tin species as the C/Sn ratio is found to be lower than 3.0 (for example, after reaction of SnMe_4 with 37.5 wt % $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ the tin and C loadings are 5.61 and 1.55 wt %, respectively, corresponding to a C/Sn ratio equal to 2.7).

The tin surface species resulting from the reaction of $\text{Sn}(\text{CH}_3)_4$ with $\text{HSiW}_{12}\text{O}_{40}/\text{SiO}_2$ were also studied by EXAFS spectroscopy. Figure 5 shows the experimental and fitted EXAFS signals. The fit (Table 1) corresponds to a first coordination sphere of about 2.7 oxygen atoms at $1.99(3)\text{ \AA}$ and 1.3 carbon atoms at $2.12(1)\text{ \AA}$ coordinated to tin which can be respectively assigned to σ -bonded siloxy ($-\text{OSi}\equiv$) and to σ -bonded carbons of methyl groups ($-\text{CH}_3$). These Sn-O and Sn-C bond lengths are the same that we found by EXAFS for Me_3SnOH in heptane ($1.99(2)\text{ \AA}$ and $2.12(1)\text{ \AA}$, respectively) and are consistent with the corresponding bond distances obtained by X-ray diffraction in a crystalline cubic, trimethyl tin functionalized

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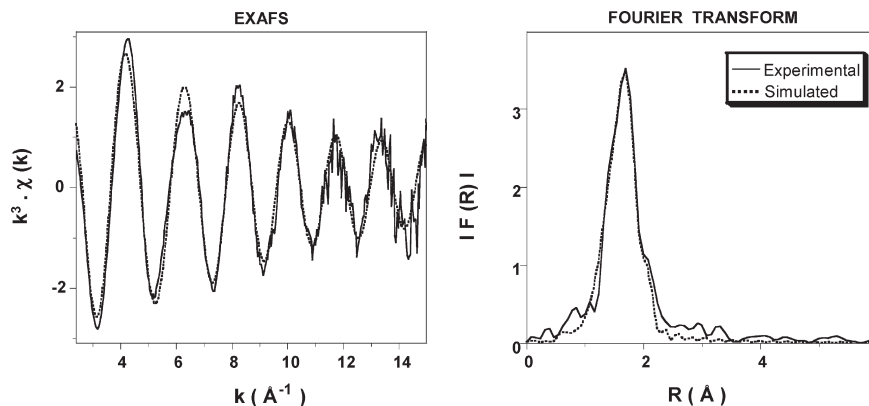


Figure 5. Sn K-edge-weighted EXAFS (left) and corresponding Fourier transform (right) for the solid $\text{Sn}(\text{CH}_3)_4/\text{SiO}_2$ and comparison to simulated curves. Solid lines, experimental; dashed lines, spherical wave theory.

Table 1. Sn K-Edge EXAFS-Derived Structural Parameters for the Grafted Species Resulting from the Reaction of $\text{Sn}(\text{CH}_3)_4$ with $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ ^{a,b}

type of neighbor	coordination number	R (Å)	D. W. (σ^2 , Å ²)
Sn—O—	2.7(6)	1.99(3)	0.009(3)
Sn—CH ₃	1.3 ^c	2.12(1)	0.001(4)
Sn—O	1.0	2.32(5)	0.008(5)

^aThe values given in parentheses represent the statistical errors generated in “RoundMidnight” (EXAFS fitting program). ^b Δk : [2.4–15.0 Å⁻¹] – ΔR : [0.8–2.8 Å]; $S_0^2 = 1.0$; $\Delta E_0 = 7.6 \pm 1.1$ eV (the same for all shells); Fit residue: $\rho = 6.1\%$; Quality factor: $(\Delta\chi^2)/\nu = 1.23$ ($\nu = 10/18$). ^cParameter constrained to the parameter above ($N_C + N_O = 4.0$).

spherosilicate $\{\text{Si}_8\text{O}_{20}(\text{Sn}(\text{CH}_3)_3)_8\}$ and a pentagonal prismatic tin-spherosilicate $\{\text{Si}_{10}\text{O}_{25}(\text{Sn}(\text{CH}_3)_3)_{10}\}$.¹² They are also in good agreement with values reported for analogous tin molecular complexes, for example, 1.986(4) Å for the Sn—OSi≡ bond length and 2.110(7) to 2.123(7) Å for the three Sn—CH₃ distances in $(\text{CH}_3)_3\text{Sn}-\text{OSi}(\text{Me})_2\text{Os}(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{CO})(\text{Cl})$;¹³ 1.990(5) to 2.006(5) Å for the shortest Sn—OSi≡ bond length and 2.093(10) to 2.113(8) Å for the Sn—CH₃ distances in a $\{[(\text{Me}_3\text{SiO})(\text{CH}_3)_2\text{Sn}]_2\text{O}\}_2$ stannasiloxane.¹⁴ One additional shell could be added to improve the fit, with one further oxygen at 2.32 Å which could correspond to a π -bonded oxygen atom of the surface ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$ siloxy bridge or a $\text{W}-\text{O}$ group arising from a $\text{W}=\text{O}$ or a $\text{W}-\text{O}-\text{W}$ of the supported HPA).

These results are in full agreement with the solid-state NMR and microanalysis data and show the presence of a mixture of mono- and digrafted species on silica.

Application to Catalysts Prepared in Different Solvents. Silica-supported heteropolyacids are usually prepared by impregnation of the support with a solution containing the desired amount of polyacid followed by elimination of the solvent by treatment at mild temperature (typically 50 to 100 °C). However, depending on the method, different dispersions of the heteropolyoxometalate on the oxide support are observed, with formation of bulk

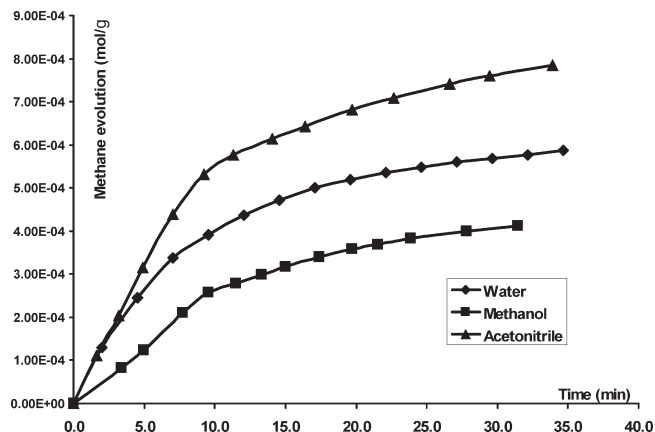


Figure 6. Methane evolution as a function of time during the reaction at 20 °C of SnMe_4 with 27.5 wt % $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ dehydroxylated at 200 °C. Effect of the solvent of preparation.

polyacid, small aggregates or isolated polyanions on the surface. This point has been emphasized several years ago and, depending on the authors, the best results were obtained with one solvent or another one (see for example refs 15 and 16). Unfortunately, it is very difficult to access from these results the best catalysts as the dispersion depends not only on the solvent but also on the treatment after the impregnation. We have shown above that the reaction of SnMe_4 with the supported heteropolyacid could be decomposed into a reaction with the acidic proton followed by a migration on the silica support. So, a different distribution of the heteropolyacid on the surface should lead to different kinetic curves for the methane evolution. Indeed, the lower the concentration of the acidic protons the lower will be the first reaction. In addition, if the polyacids are not well dispersed on the surface but present as aggregates even if these aggregates have the same number of acidic protons as isolated species, this will have an effect on the second reaction as the migration on the silica surface will occur slower than on a well-dispersed catalyst, the mean distance to pass being higher. As an example Figure 6 shows the curves obtained for $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (27.5 wt % loading)

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prepared in three different solvents, methanol, acetonitrile and water, all other preparation conditions being the same. It can be seen that acetonitrile is the best solvent followed by water, methanol leading to the smallest methane evolution. We can then conclude that, *in our conditions*, acetonitrile leads to the best dispersion on the silica support.

Conclusion

We have shown that tetramethyltin reacts at room temperature, as in solution, with the strong acid sites of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ supported on silica with evolution of methane and formation of a trimethyltin fragment. However, this fragment, which is not stabilized by the oxygen atoms of the polyoxometalate because of their low nucleophilicity, migrates on the silica support. It reacts then with a surface silanol group restoring the strong acid site on the polyoxometalate leading to $\equiv\text{Si}-\text{O}-\text{SnMe}_3$ as observed on silica alone after reaction at 150 °C. This surface complex can further react with the strong acid site of the polyoxometalate, leading to the formation of bigrafted species. This reaction can give informations on the solid and on the dispersion of the polyoxometalates, as the kinetics of the reaction will depend on the distance between the silanol groups and the polyoxometalate and on their density. Further work is in progress to better understand this phenomenon.

Experimental Section

Materials. Tetramethyltin was purchased by Aldrich. It was dried over molecular sieves and degassed before use. ^{13}C enriched tetramethyl tin was synthesized according to ref 17 by using $^{13}\text{CH}_3\text{MgI}$. The silica used for these studies was Aerosil silica ($S = 200 \text{ m}^2 \text{ g}^{-1}$). The heteropolyacid was deposited on the silica support by using a classical impregnation technique in water.

Kinetic Studies. For the kinetic studies the supported heteropoly acid (between 250 mg and 1 g) was introduced into a sealed glass high vacuum reactor of known volume equipped with CaF_2 windows. The powder was then treated during 2 h at 200 °C under high vacuum (10^{-5} torr). After cooling to room temperature a large excess of tetramethyltin (typically 0.2 mL) was added, and infrared spectra of the gas phase recorded as a function of time. The amount of evolved methane was quantified by integration of the region between 3126.10 and 3101.51 cm^{-1} .

Solid State NMR. $1\text{D } ^1\text{H}$, ^{13}C and ^{119}Sn MAS NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300.18, 75.47, and 111.88 MHz respectively. The samples were introduced under argon in a zirconia rotor, which was then tightly closed. For all experiments the rotation frequency was set to 10 kHz. ^1H and ^{13}C chemical shifts are given with respect to TMS as an external standard (precision 0.2 and 0.5 ppm, respectively). ^{119}Sn chemical shifts are given with respect to SnMe_4 (precision 1 ppm). ^{13}C NMR spectra were recorded using cross-polarization from protons (contact time 2 ms), while ^{119}Sn ones were obtained after direct irradiation of the tin nuclei. In the two cases the spectra were recorded with proton decoupling. The 2D $^1\text{H}-^{13}\text{C}$ HETCOR experiments were performed on a ^{13}C enriched sample. Two experiments were made, one with a short contact time (200 μs) for the detection of direct C–H

bonds and one with a large contact time (5 ms) for the detection of correlations at higher distances.

EXAFS Experiments. EXAFS data were acquired on the beamline BM29 at the ESRF (Grenoble, France) at the Sn K-edge, between 28.8 and 30.3 keV, in the transmission mode, using a double crystal monochromator, Si(111), detuned to minimize higher harmonics and ionization chambers as detectors. The calibration in energy was performed with a tin foil ($E_0 = 29,200 \text{ eV}$). The samples were introduced, within a dry and air-preserved glovebox, into a double airtight cell equipped with Kapton windows. The EXAFS spectra were analyzed by standard procedures using the program Athena¹⁸ and the suite of programs developed by Alain Michalowicz, in particular the EXAFS fitting program RoundMidnight using calculations with spherical waves.^{19,20} The postedge background subtraction was carefully conducted using polynomial or cubic-spline fittings, and the removal of the low-frequency contributions was checked by further Fourier transformation. The fitting of the spectrum was done with the k^3 weighted data using the following EXAFS equation, where S_0^2 is a scale factor; N_i is the coordination number of shell i ; r_c is the total central atom loss factor; F_i is the EXAFS scattering function for atom i ; R_i is the distance to atom i from the absorbing atom; λ is the photoelectron mean free path; σ_i is the Debye–Waller factor; Φ_i is the EXAFS phase function for atom i ; and Φ_c is the EXAFS phase function for the absorbing atom:

$$\chi(k) \cong S_0^2 r_c(k) \sum_{i=1}^n \frac{N_i F_i(k, R_i)}{k R_i^2} \exp\left(\frac{-2R_i}{\lambda(k)}\right) \exp(-2\sigma_i^2 k^2) \sin[2kR_i + \Phi_i(k, R_i) + \Phi_c(k)]$$

The program FEFF8²¹ was used to calculate theoretical values for r_c , F_i , λ , and $\Phi_i + \Phi_c$ based on model clusters of atoms. The refinements were performed by fitting the structural parameters N_i , R_i , σ_i , and the energy shift, ΔE_0 (the same for all shells). The fit residue, ρ (%), was calculated by the following formula:

$$\rho = \frac{\sum_k [k^3 \chi_{\text{exp}}(k) - k^3 \chi_{\text{cal}}(k)]^2}{\sum_k [k^3 \chi_{\text{exp}}(k)]^2} \times 100$$

As recommended by the Standards and Criteria Committee of the International XAFS Society,²² an improvement of the fit took into account the number of fitted parameters. The number of statistically independent data points or maximum number of degrees of freedom in the signal, is defined as $N_{\text{idp}} = (2\Delta k \Delta R / \pi) + 2$.

The inclusion of extra parameters were statistically validated by a decrease of the quality factor, $(\Delta\chi)^2/\nu$ and the values of the statistical errors generated in RoundMidnight were multiplied by $[(\Delta\chi)^2/\nu]^{1/2}$ to take the systematic errors into account, since the quality factors exceeded 1. The error bars thus calculated are given in parentheses after each refined parameter. The scale factor, $S_0^2 = 1.0$ was determined from the analysis of the spectra of reference compounds, Me_3SnOH diluted in heptane (1 O at 1.99(2) Å and 3C at 2.12(1) Å), SnBu_4 in heptane (4 C at 2.15(1) Å). This factor was kept constant in all the fits.

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