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Supplementary materials

Ethoxy and silsesquioxane derivatives of antimony as dopant precursors: unravelling the structure and thermal stability of surface species on SiO_2

T. Alphazan,[a,b] P. Florian[c] and C. Thieuleux[b,*]

a. Univ. Grenoble Alpes, FR-38000 Grenoble, CEA, LETI, Minatec Campus, FR-38054 Grenoble Cedex 9, France

b. C2P2, CPE Lyon, 43 Bd du 11 Nov. 1918, 69616 Villeurbanne cedex France

c. Conditions Extrêmes et Matériaux: Haute Température et Irradiation, CNRS-UPR 3079, 1 d Avenue de la Recherche Scientifique, 45071 Orléans, Cedex 2, France

Outline

SI 1. General procedures and methods

All experiments, otherwise stated, were carried out under dry and oxygen free Ar atmosphere using either standard Schlenk or glovebox (GB) techniques for the organic synthesis. For syntheses and treatments of surface species, reactions were carried out using high vacuum lines (10^{-5} mbar). Elemental analyses of supported materials were performed at “Mikroanalytisches Labor Pascher” in Germany. High resolution mass spectroscopy (HR-MS) was performed with a micrOTOF-Q II from Bruker, in ESI+ mode. Toluene and pentane were dried using an MBraun solvent purification system, contacted with molecular sieves 4 Å and degassed under vacuum. Hepta-isobutyl-POSS triol (POSS-OH), antimony(III) chloride ($SbCl_3$), antimony(III) ethoxide ($[Sb(OEt)_3]_2$) and triethylamine (Et_3N) were purchased from Sigma Aldrich. Et_3N was distilled over CaH_2 prior to use. $[Sb(OEt)_3]_2$ was distilled under reduced pressure to give a colourless, moisture sensitive liquid stored in the glovebox.

FTIR and in-situ FTIR coupled with GC/MS. FTIR spectra recorded in diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) mode were obtained on a Nicolet 6700 FT-IR spectrometer equipped with a HgCdTe (MCT) detector cooled with liquid N_2. The samples were loaded into a custom DRIFT cell equipped with CaF_2 windows (or ZnSe for in-situ experiments) under inert atmosphere (glovebox). Typically, 64 scans were acquired (4 cm^{-1} resolution). For in-situ experiments, 4 spectra per minute were acquired in average; materials were decomposed under a flux (10 $ml.min^{-1}$) of dry gas (air or N_2), with a heating rate of 6°C.min^{-1}, from ~20°C to 500°C (or 650°C), and maintained at the desired temperature before being cooled. Gases, released during thermal treatment, were collected and analyzed by GC/MS for identification.

Liquid state NMR. Liquid-state NMR spectra were recorded using a Bruker Spectrospin 300 MHz spectrometer. ^{1}H, ^{13}C and chemical shifts were referenced to TMS at 0 ppm.

Solid-state NMR. 40 to 50 mg of material was packed in 4.0 mm zirconia NMR rotor under inert atmosphere. NMR spectra were acquired either on a 300 MHz or 500 MHz ultrashieldedBruker NMR spectrometer.^{1}H, ^{13}C and ^{29}Si spectra were recorded using a 4.0 mm cross-polarization (CP) magic angle spinning (MAS) probe with a sample temperature of 294 K and sample spinning frequencies between 5 to 10 kHz. Standard CP was used to record ^{29}Si and ^{13}C spectra. ^{1}H, ^{13}C and chemical shifts were referenced to TMS at 0 ppm. ^{121}Sb NMR spectra were obtained on a Bruker Avance III 850 spectrometer operating at 20.0T (203.5MHz for ^{121}Sb) and using a “low-gamma” 4mm MAS probe under static conditions with radio-frequency fields of 80kHz.

*Thermogravimetric analysis (TGA).*TGA experiments were performed on a Mettler DSC/TGA StarSyst apparatus. 10 mg of material were loaded in a sealed aluminium pan under inert atmosphere. Analyses were performed under a flux (10 ml.min^{-1}) of gas (air, N_2), from ~20°C to 500°C (6°C.min^{-1}), then at 500°C (isotherm) for 90 min.

Differential scanning calorimetry (DSC). DSC experiments were performed on a Mettler DSC 2 StarSyst apparatus, using the same parameters as for TGA.

*Synthesis of hepta-isobutyl-polyhedral oligomeric silsesquioxane antimony triester (**POSS-Sb**)*. POSS-Sb was prepared as described in the main text. **Yield**: 55% (1.42 g). **^{1}H NMR**, **^{13}C NMR** and **^{29}Si NMR**: see main text. **^{121}Sb NMR** (ppm): *very broad signal*. **HR-MS**: m/z $[M+H]^+$= 909.1803 (expected for $C_{28}H_{64}O_{12}Si_7Sb$: 909.1815). **XRD**: Monocrystals were grown by slow evaporation of a toluene solution, or at low temperature (-30 °C) in GB. However, no structure resolution was possible.

Antimony(III) ethoxide. Commercial $Sb(OEt)_3$ [sigma] was a redish liquid. Distillation under a slightly reduced pressure (Schlenk line) at about 70°C gave a colorless liquid, highly moisture and O_2 sensitive, that was stored in GB. **^{1}H NMR** (C_6D_6, 25 °C, ppm): δ_H= 4.02 (q, 2H, $C\mathit{H}_2CH_3$), 1.23 (t, 3H, $CH_2C\mathit{H}_3$).**^{13}C NMR** (ppm): δ_C= 58.9 ($\mathit{C}H_2CH_3$), 20.2 ($CH_2\mathit{C}H_3$). **IR** (cm^{-1}): 2967, 2921, 2866 ν(C-H); 2746, 2715 (s, 2xδ(C-H)); 2610 (vw); 1925 (vw); 1477, 1442, 1380, 1359 δ(C-H);1284 (vw), 1155, 1094 C-H; 1041 ν_{as}(CCO); 891 ν_s(CCO); 805 (vw); 550 (broad) ν(Sb-O)[1,2]

Study on silica nanoparticles (NPs).

Preparation of partially dehydroxylated silica at 700 °C ($SiO_{2-(700)}$). Silica powder (see main text) was calcined for 5 h under air at 500 °C (6 °C.min^{-1}), partially dehydroxylated at 500°C in secondary vacuum (10^{-5} mbar) for 12 h, then at 700 °C for 10 h, and finally stored in the glovebox. S_{BET} ($m^2.g^{-1}$): 197. IR (cm^{-1}): 3747 (isolated SiOH), 3600 (large peak, very low intensity, bonded SiOH).

Quantification of surface SiOH groups ($OH.nm^{-2}$) found onto SiO_2. The procedure was described elsewhere.[3]

Preparation of ^{18}O-doped $SiO_{2\text{-}(700)}$. The procedure, using a vapor pressure of $H_2{}^{18}O$ and $SiO_{2\text{-}(700)}$, was described elsewhere.[4]

*Grafting **POSS-Sb** onto $SiO_{2\text{-}(500)}$. Representative procedure.* POSS-Sb (468 mg, 5.1×10^{-4} mol, 0.7 eq) was solubilized in pentane (10 mL) and was subsequently contacted with $SiO_{2\text{-}(500)}$ (~1.0 g, ~7.3×10^{-4} mol surface silanol) at 25 °C for 2.5 h, under gentle stirring. After filtration, the solid was washed 3 times with pentane, and all volatile compounds were removed *in vacuo (10^{-3} mbar)*. The resulting solid **POSS-Sb/$SiO_{2\text{-}(500)}$** was dried under high vacuum (10^{-5} mbar) and the grafted species were then stored under Argon. **IR** (cm^{-1}): 3746 (remaining isolated SiOH), 3702 (perturbed, H-bonded SiOH), 3364 (broad), 2960, 2933, 2908 & 2875 ν(C-H), 2782, 2724, 2629 (probable combination bands or overtones of CH groups), 1468 & 1403 δ(C-H). **^1H MAS NMR** (ppm): δ_H= 1.8 ($CH_2C\mathit{H}(CH_3)_2$), 0.9 ($C\mathit{H_2}CH(CH_3)_2$ and $CH_2CH(C\mathit{H_3})_2$). **^{13}C NMR** (CP-MAS, ppm): δ_C= 24 (broad). **^{29}Si NMR** (HP-Dec, ppm): δ_{Si}= –57 (~1 Si, T_2-SiOH, POSS cage), –66 (6 Si, T_3-type, POSS cage), *ca.* –108 (broad, Q-type Si, SiO_2 network). **Elemental analysis**: 3.16 wt % C, 0.60 wt % H, 1.09 wt % Sb, *i.e.* H/C(at/at)= 2.3, C/Sb= 29.4 and 0.27 Sb/nm² corresponding to ~14% grafting. Expected for (≡Si-O)$SbC_{28}H_{64}O_{12}Si_7$: H/C(at/at)= 2.3, C/Sb= 28.0. **Misc**: Only pure POSS-Sb was recovered from the solution after grafting/rinsing.

*Grafting **POSS-Sb** onto $SiO_{2\text{-}(700)}{}^{18}O$-doped.* POSS-Sb/$Si^{18}O_{2\text{-}(700)}$ was prepared according to the representative procedure, with 215 mg of $Si^{18}O_{2\text{-}(700)}$ (~5.0×10^{-5} mol surface silanols) and 52 mg of POSS-Sb (5.7×10^{-5} mol, 1.1 eq). **IR** (cm^{-1}): 3745 (remaining isolated $Si^{16}OH$), 3734 (remaining isolated $Si^{18}OH$), 3699 (perturbed, H-bonded SiOH), 3363 (broad), 2960, 2933, 2908 & 2875 v(C-H), 2782, 2724, 2629 (probable combination bands or overtones of CH groups), 1468 δ(C-H).

Grafting ***POSS-Sb*** *onto $SiO_{2-(140)}$.* POSS-Sb/$SiO_{2-(140)}$ was prepared according to the representative procedure, with 330 mg of $SiO_{2-(140)}$ (~5.0 × 10^{-4} mol surface silanols) and 206 mg of POSS-Sb (2.3 × 10^{-4} mol, 0.5 eq). **IR** (cm^{-1}): 3741 (remaining isolated SiOH), 3696 (perturbed, H-bonded SiOH), 3450 (broad), 2958, 2943, 2906 & 2875 v(C-H), 2782, 2728, 2628 (probable combination bands or overtones of CH groups), 1468 δ(C-H). **^{1}H MAS NMR** (ppm): δ_H= 1.9 ($CH_2C\mathit{H}(CH_3)_2$), 0.9 ($C\mathit{H_2}CH(CH_3)_2$ and $CH_2CH(C\mathit{H_3})_2$). **^{13}C NMR** (CP-MAS, ppm): δ_C= 24 (broad). **^{29}Si NMR** (HP-Dec, ppm): δ_{Si}= –57 (~2.5 Si, T_2-SiOH, POSS cage), –66 (T_3-type, POSS cage), *ca.* –109 (broad, Q-type Si, SiO_2 network). **Elemental analysis**: 4.20 wt % C, 0.88 wt % H, 1.53 wt % Sb, *i.e.* H/C(at/at)= 2.5, C/Sb= 28.0 and 0.38 Sb/nm² corresponding to ~9% grafting. Expected for $(\equiv Si-O)_2SbC_{28}H_{65}O_{12}Si_7$: H/C(at/at)= 2.3, C/Sb= 28.0. **Misc**: Only pure POSS-Sb was recovered from the solution after grafting/rinsing.

Grafting ***$[Sb(OEt)_3]_2$*** *onto $SiO_{2-(500)}$.* $[Sb(OEt)_3]_2$/$SiO_{2-(500)}$ was prepared according to the representative procedure, with ~120 µl (~7.1 x 10^{-4} mol, 1.2 eq) of $[Sb(OEt)_3]_2$ and 766 mg of $SiO_{2-(500)}$ (~5.6 x 10^{-4} mol surface silanol) at 25 °C. **IR** (cm^{-1}): 3664 (perturbed, H-bonded SiOH), 2972, 2929, 2889 & 2875 v(C-H), 2752, 2723, 2704 (probable combination bands or overtones of CH groups), 2614 (already observed in the starting compound), 1478, 1445 & 1385 δ(C-H). **^{1}H MAS NMR** (ppm): δ_H= 3.9 ($C\mathit{H_2}CH_3$), 1.1 ($CH_2C\mathit{H_3}$). **^{13}C NMR** (CP-MAS, ppm): δ_C= 58 ($\mathit{C}H_2CH_3$), 17 ($CH_2\mathit{C}H_3$). **Elemental analysis**: 2.78 wt % C, 0.56 wt % H, 7.21 wt % Sb, *i.e.* H/C(at/at)= 2.4, C/Sb= 3.9 and

1.8 Sb/nm² corresponding to ~90% grafting. Expected for $(\equiv Si\text{-}O)Sb(OEt)_2$: H/C(at/at)= 2.5, C/Sb= 4.0.

SI 2. DSC analysis of POSS-triol, POSS-P and POSS-Sb

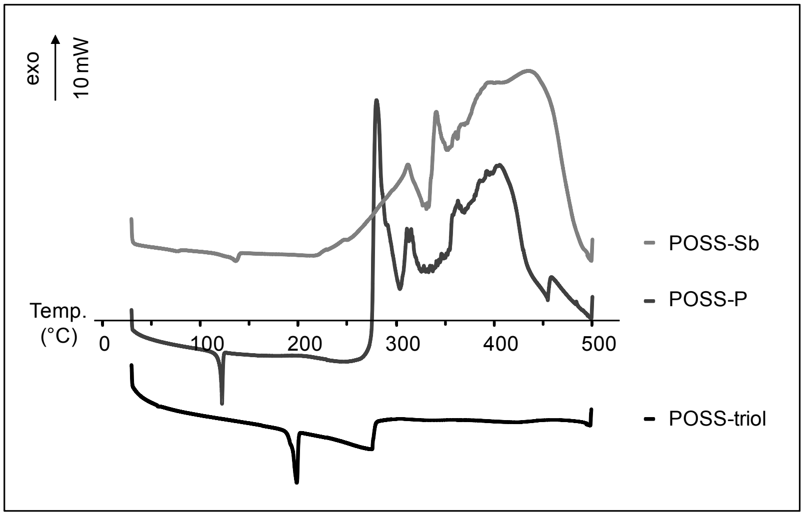

Figure S2: DSC traces of POSS-triol, POSS-P and POSS-Sb under nitrogen, between 30°C and 500°C, 6°C/min.

In our conditions, DSC analyses performed in N_2 reveal that the starting POSS cage melts at 198°C (-32.3 kJ/mol) while POSS-Sb and POSS-P melt at 136°C (-32.9 kJ/mol) and 122°C (-21.5 kJ/mol), respectively

SI 3. TGA analysis of POSS-triol, POSS-P and POSS-Sb

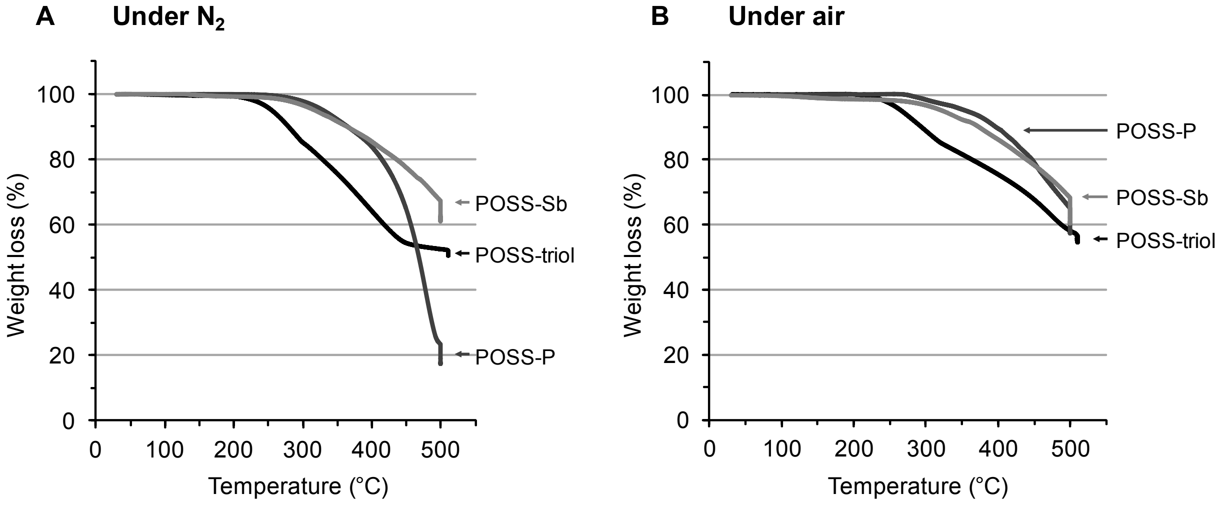

Figure S3: TGA traces of POSS-triol, POSS-P and POSS-Sb under nitrogen (A) and under air (B), between ~30°C and 500°C (90 min at 500°C), 6°C/min.

SI 4. Thermal stability of molecular POSS-Sb followed by in-situ IR

General comments: due to melting of POSS-Sb, IR (DRIFT) spectra of poor quality were obtained above 150°C and more. Experiments were performed up to 650°C under N_2, and 500°C under air, due to apparatus specifications. Only spectra recorded at ~20°C, before and after thermal treatment, are provided in the main manuscript.

SI 5. ^{29}Si CPMAS NMR spectra of SiO_2 -supported POSS-Sb materials

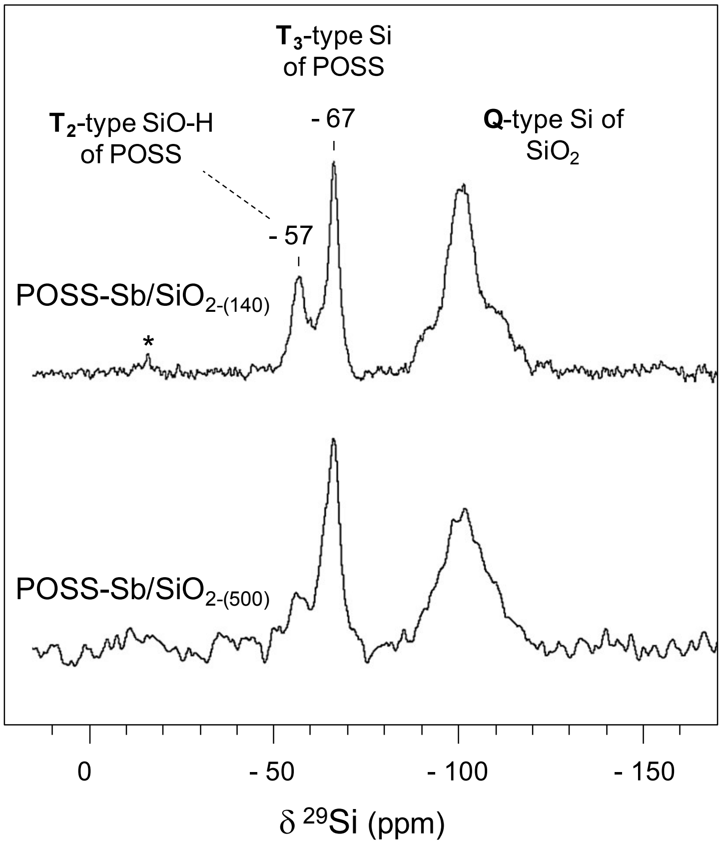

Figure S5: ^{29}Si CPMAS NMR spectra of SiO_2 -supported POSS-Sb materials obtained at 11.7 T, with $\omega_{rot}/2\pi$ = 5 KHz, 45 k scans, a recycle delay of 5 s, and a contact time of 2 ms. * denotes spinning side bands.

SI 6: Differential IR spectra of SiO_2 supported POSS-Sb materials

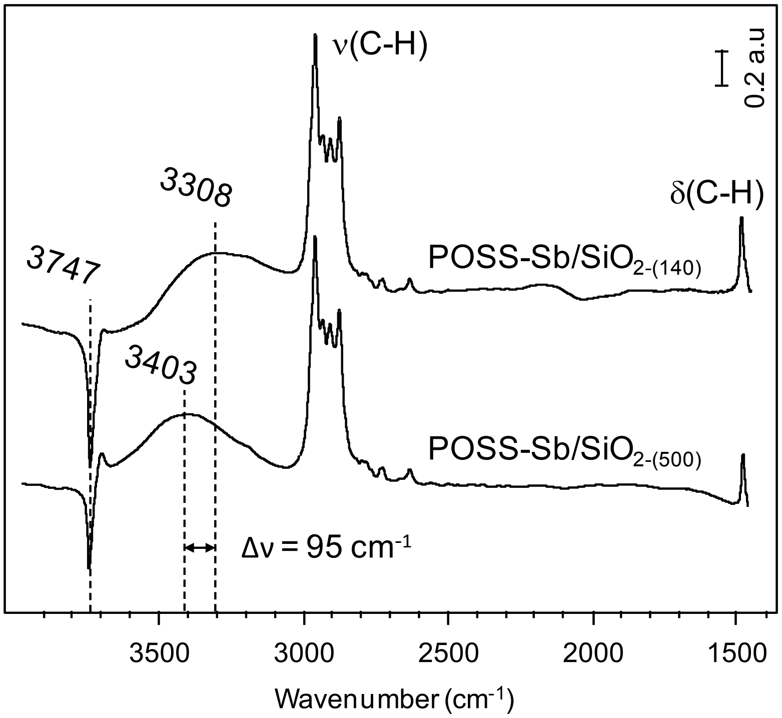

Figure S6: Differential IR spectra of SiO_2 supported POSS-Sb materials, referenced to their corresponding silica support, partially dehydroxylated at 500°C or dehydrated at 140°C.

Negative bands ~3747 cm^{-1} are assigned to isolated silanol that have been consumed upon grafting.

Positive bands located between 3000-2850 cm^{-1} and located at 1467 cm^{-1} are ascribed to C-H bonds of iBu groups of POSS.

Positive bands observed at 3403 and 3308 cm^{-1} are tentatively assigned to SiO-H bonds of T_2-type SiOH groups formed on POSS upon grafting of POSS-Sb.

SI 7. IR (DRIFT) spectra of ^{18}O-doped $SiO_{2-(700)}$ and related Sb-material

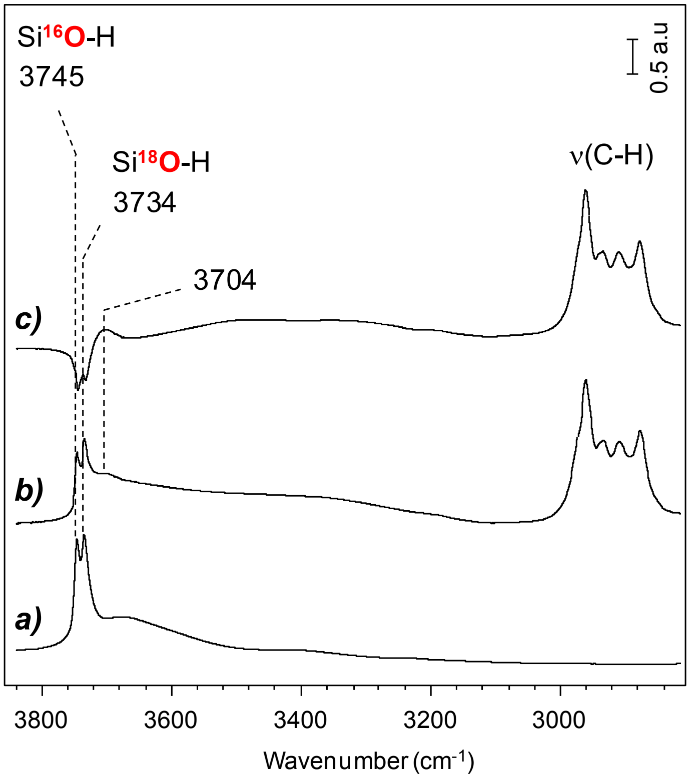

Figure S7: IR (DRIFT) spectra of ^{18}O-doped $SiO_{2-(700)}$ (a) and the supported POSS-Sb material (b). Differential IR spectrum, referenced to ^{18}O-doped $SiO_{2-(700)}$ (c).

SI 8.^{1}H MAS and ^{13}C CPMAS NMR spectra of $[Sb(OEt)_3]_2/SiO_{2-(500)}$

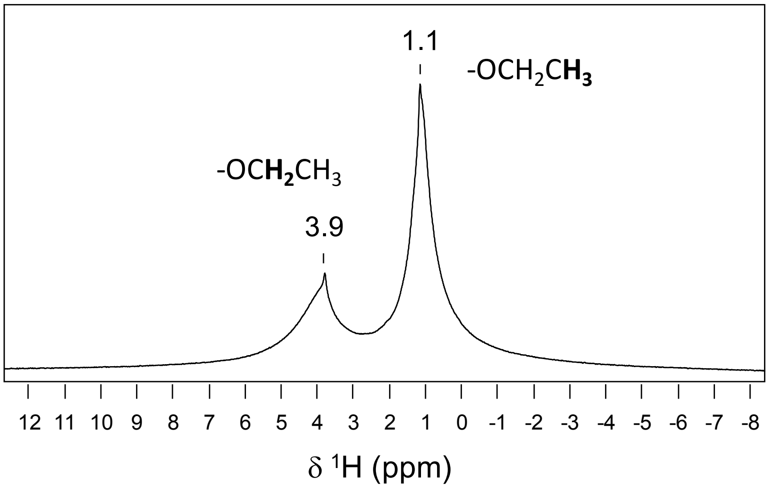

Figure S8-A: ^{1}H MAS NMR spectrum of $[Sb(OEt)_3]_2/SiO_{2-(500)}$ obtained at 11.7 T, with $\omega_{rot}/2\pi$ = 10 KHz, 8 scans, and recycle delay of 5 s

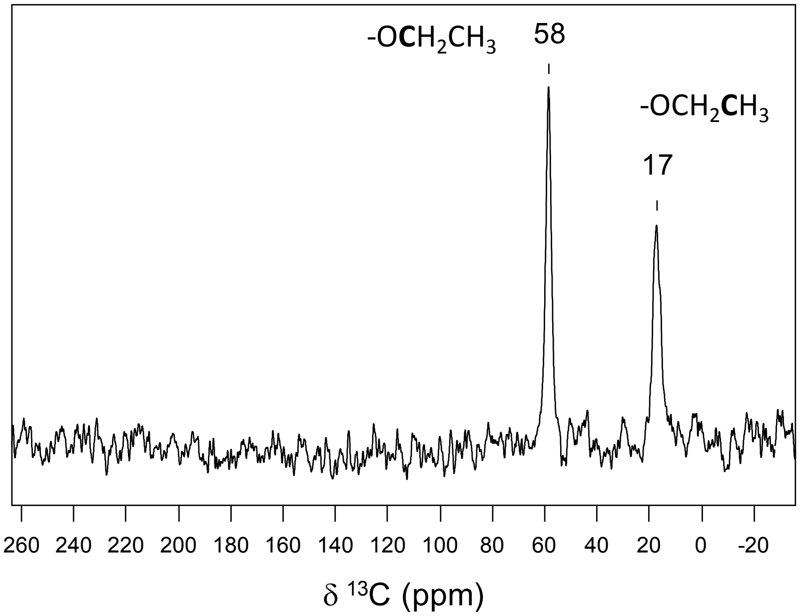

Figure S8-B: ^{13}C CPMAS NMR spectrum of $[Sb(OEt)_3]_2/SiO_{2-(500)}$, obtained at 11.7 T, with $\omega_{rot}/2\pi$ = 10 KHz, 2 k scans, a recycle delay of 30 s, and a contact time of 2 ms

SI 9. ^{121}Sb NMR spectra of POSS-Sb and $[Sb(OEt)_3]_2$

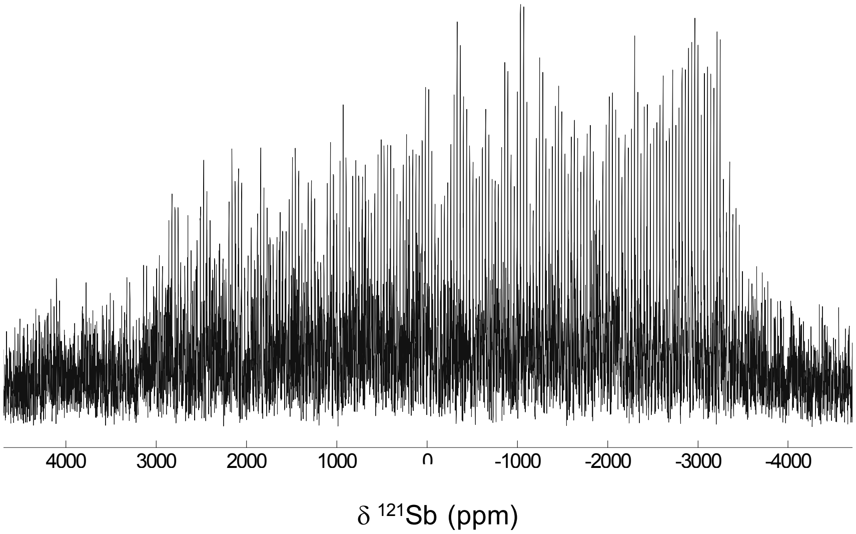

Figure S9-A:^{121}Sb QCPMG-WURST NMR spectrum of POSS-Sb obtained at 20.0T with 200 k scans, with a recycle delay of 0.3s (i.e. 17 h of acquisition time) and a WURST shape irradiating over 2MHz.

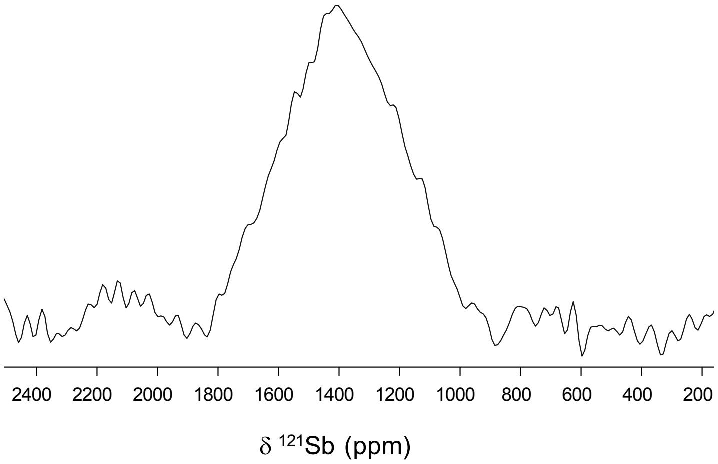

Figure S9-B:^{121}Sb single-pulse NMR spectrum of (liquid) $[Sb(OEt)_3]_2$, obtained at 20.0 T, with 512 scans, a recycle delay of 0.3 s, and using a 90° pulse at a radio-frequency field of 80kHz.

Comments:^{121}Sb is a quadrupolar nuclei, associated with a very large quadrupolar constant, thus making ^{121}Sb NMR spectra difficult to record (extremely wide line shapes potentially spreading over several MHz combined with possibly short relaxation times T_2) even for symmetric hexacoordinated compounds such as nearly octahedral $KSb(OH)_6$, used as reference.[5] Here, the large ^{121}Sb signal obtained for the molecular compound **POSS-Sb** (2 MHz, Figure S9-A) extends over at least 1.3MHz, i.e. approximately three times more than the spectra obtained for $KSb(OH)_6$ by Faucher et al. at an equivalent magnetic field. This result probably originates from the pseudo-trigonal symmetry of the Sb center in POSS-Sb,[6,7] thus increasing Sb quadrupolar constant and broadening the NMR signal, which –along with a short T_2– prevents recording good quality spectra at room temperature within reasonable acquisition time even using a QCPMG-WURST acquisition sequence[8] (the signal disappeared within the noise in less than 2 ms within the QCPMG sequence). Besides, ^{121}Sb NMR analysis was intended on $[Sb(OEt)_3]_2$ and confirmed the difficulties to record NMR of quadrupolar nuclei in structure of lower symmetry..[9] Considering these results, we did not try to analyze SiO_2-supported materials as they contain at least 10 times less Sb than molecular compounds and would require too long acquisition time.

SI 10. Decomposition of $[Sb(OEt)_3]_2/SiO_{2\text{-}(500)}$ followed by *in-situ* IR-GC/MS

General comments: Experiments were performed up to 650°C under N_2, and 500°C under air, due to apparatus specifications.

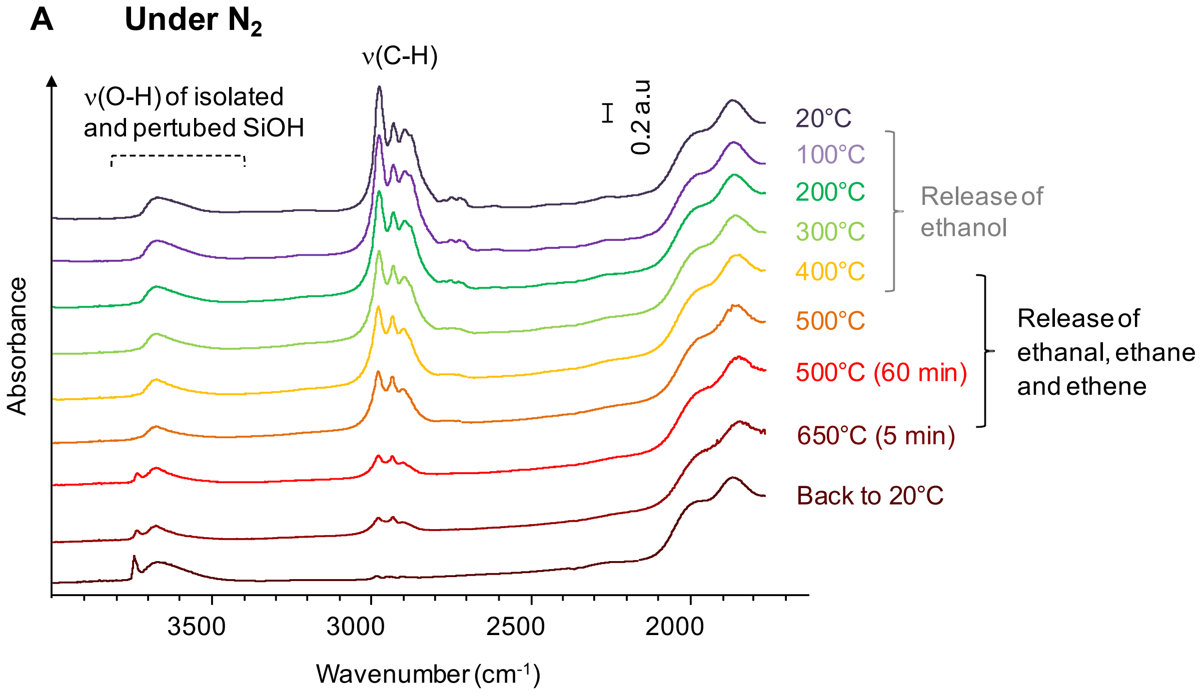

Figure S10-A: IR (*in-situ* DRIFT) spectra of $[Sb(OEt)_3]_2/SiO_{2\text{-}(500)}$ material, heated from 20°C to 500°C and 650°C (6°C/min), under N_2 (10 mL/min).

Comments: The ν(C-H) modes significantly decrease above 400°C, consistent with the release of several C_2 compounds detected by GC/MS. Besides, the similar intensity of these CH features between 20°C and 350°C suggests that ethanol, released from about 60°C (GC/MS), probably comes from little decomposition of surface species, or traces of physisorbed EtOH. Note also the appearance, from 500°C, of a band at 3744 cm^{-1}, which is assigned to isolated SiOH groups, and which thus highlights a modification of the silica surface, probably linked to the decomposition of surface species. Only negligible CH bands remains after thermal treatment.

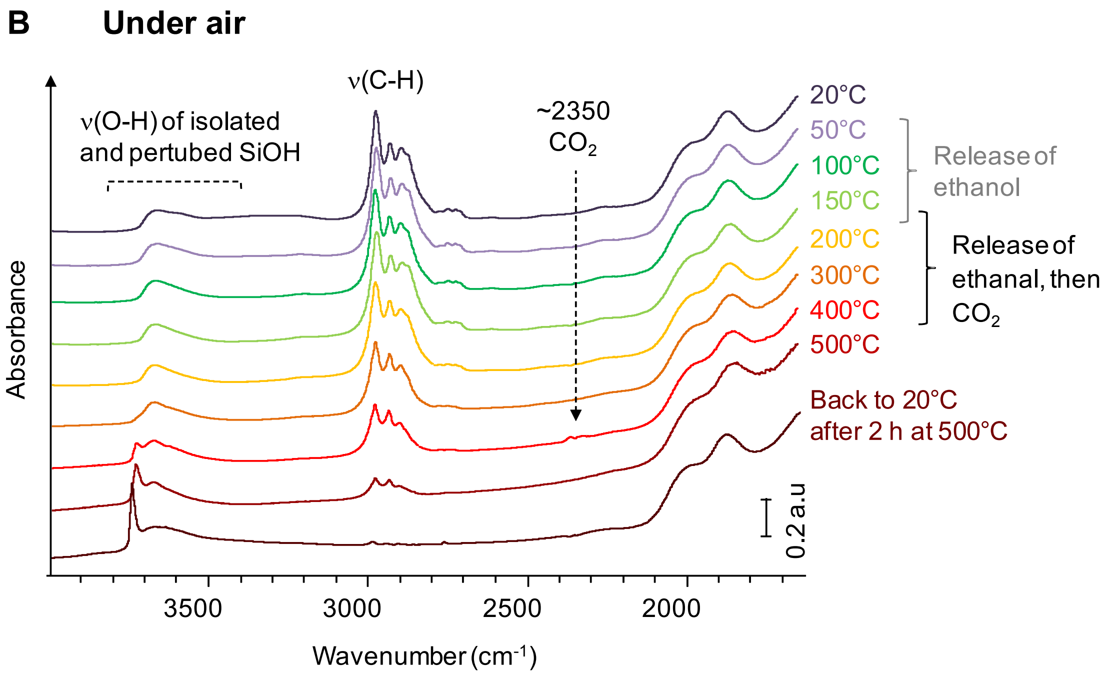

Figure S10-B: IR (*in-situ* DRIFT) spectra of $[Sb(OEt)_3]_2/SiO_{2-(500)}$ material, heated from 20°C to 500°C (6°C/min), under air (10 mL/min).

Comments: The ν(C-H) modes significantly decrease above 200°C, consistent with the release of ethanal, detected by GC/MS. As for the similar experiment under N_2, the similar intensity of the C-H features between 20°C and 200°C suggests that ethanol, released from about 60°C (GC/MS), probably comes from little decomposition of surface species when contacted with air, or traces of physisorbed EtOH. Note also the appearance of a v(SiO-H) band (3744 cm^{-1}) assigned to isolated SiOH between 300°C and 400°C, as well as a v(C=O) band, consistent with the calcination of organic groups by O_2, and a release of CO_2 and H_2O. Only negligible CH bands remains after thermal treatment.

SI 11. References

1 G. E. Binder, U. Ensinger, W. Dorsch and A. Schmidt, *Z. Für Anorg. Allg. Chem.*, 1983, **507**, 163–170.
2 Y. Kawasaki, Y. Yamamoto and M. Wada, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 145–148.
3 T. Alphazan, L. Mathey, M. Schwarzwälder, T.-H. Lin, A. J. Rossini, R. Wischert, V. Enyedi, H. Fontaine, M. Veillerot, A. Lesage, L. Emsley, L. Veyre, F. Martin, C. Thieuleux and C. Copéret, *Chem. Mater.*, 2016, **28**, 3634–3640.
4 L. Mathey, T. Alphazan, M. Valla, L. Veyre, H. Fontaine, V. Enyedi, K. Yckache, M. Danielou, S. Kerdiles, J. Guerrero, J.-P. Barnes, M. Veillerot, N. Chevalier, D. Mariolle, F. Bertin, C. Durand, M. Berthe, J. Dendooven, F. Martin, C. Thieuleux, B. Grandidier and C. Copéret, *J. Phys. Chem. C*, 2015, **119**, 13750–13757.
5 A. Faucher, V. V. Terskikh and R. E. Wasylishen, *Solid State Nucl. Magn. Reson.*, 2014, **61–62**, 54–61.
6 F. J. Feher and T. A. Budzichowski, *Organometallics*, 1991, **10**, 812–815.
7 Note: POSS-Sb crystallizes as poorly diffracting crystals from various solvents, thus preventing any crystal structure resolution. The disorder between isobutyl chains probably explains the poorly diffracting nature of these crystals.
8 L. A. O’Dell and R. W. Schurko, *Chem. Phys. Lett.*, 2008, **464**, 97–102.
9 J. Autschbach, S. Zheng and R. W. Schurko, *Concepts Magn. Reson. Part A*, 2010, **36A**, 84–126.