Surface Organometallic Chemistry of Tin: Grafting Reaction of $Sn(CH_3)_4$ in HY Zeolite Supercage

Xuxu Wang,* Huixia Zhao, Frédéric Lefebvre,† and Jean-Marie Basset†
Chemistry Department, Fuzhou University, Fuzhou 350002, P. R. China
†*Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, 43,*
Bd. du 11 Novembre 1918, 69616, Villeurbanne Cedex, France

(Received July 10, 2000; CL-000660)

Tetramethyltin reacts rapidly, even at low temperature, with the hydroxy groups in the supercages of HY zeolite, resulting in the formation of well-defined $–Sn(CH_3)_3$ fragments in the supercages. This reaction is very selective as there is no reaction with the hydroxy groups in the sodalite cages and prisms.

Surface organometallic chemistry is a rapidly growing research field whose purpose is the study of the grafting reaction of organometallic complexes onto surfaces for the acquisition of well-defined materials which could then be used in catalysis.[1] The grafting reaction of some tin complexes on various surfaces had been investigated, for example, on Aerosil silica,[2] on the silanol groups present on the external surface of mordenite[3] and the gallium and phosphorus hydroxy groups in the channels of cloverite.[4] All of the reaction mechanisms were interpreted by assuming that electrophilic attack of the hydroxy groups on the Sn–C bonds leads to the formation of trialkyltin complexes linked covalently to the surface via one oxygen atom.[5,6] Depending on the support, the reaction occurred at various temperatures: 423 K on silica and on the external silanols of mordenite, slightly at 298 K on the phosphorus hydroxy groups and at 373–423 K on the gallium hydroxy groups of cloverite. These temperatures seem to be correlated to the acidity of the corresponding hydroxy groups, higher the acidity, lower the reaction temperature. We imagined then choosing another solid, displaying acidic properties greater than those of the above ones, in order to see if this hypothesis is true and thus if a new surface species is obtained.

Y zeolite, which has highly acidic hydroxy groups and extensive use, was chosen for this objective. However most alkyltin complexes are too big to enter into the zeolite channels, avoiding such a reaction to occur. We choose then tetramethyltin, in order to ensure a good diffusion of the organometallic complex through the entire crystal (the kinetic diameter of this molecule is 0.7 nm while the diameter of the windows openings of the supercages is 0.75 nm). If the above-mentioned rule is correct, then we will obtain a new modified material containing organotin species in its channels.

The Y zeolite used was purchased from Aldrich. Its crystallinity was checked by X-ray powder diffraction while its Si/Al ratio (2.2) and the absence of extraframework aluminum were determined by ^{29}Si and ^{27}Al MAS NMR respectively. The starting zeolite, in its sodium form, was first transformed into its ammonium form by exchanging the Na^+ ions by NH_4^+ ones 6 times with NH_4Cl aqueous solution. Tetramethyltin was also purchased from Aldrich and was dried using 4A molecular sieves. The grafting reaction was performed in glassware equipment connected to a vacuum line. The NH_4Y zeolite was first treated under flowing oxygen at 400 °C during 10 h and then under vacuum (10^{-4} Pa) at the same temperature during 2 h. After this treatment all nitrogen had been removed from the solid (as indicated by chemical analysis and infrared spectroscopy) without destruction of the structure (as checked by solid-state NMR and X-ray powder diffraction). The zeolite could then be considered as a pure HY sample. After isolation and cooling at 77 K, a large excess (about 2 moles of complex per mole of protons in zeolite) of tetramethyltin was introduced onto the zeolite with a syringe via a septum. The system was then kept at the desired temperature (room temperature or lower temperature by use of a thermostatic bath). Intermittently, a trap with liquid nitrogen was used to ensure a good contact between the zeolite and the organometallic complex. The gases evolved during the reaction were analyzed qualitatively and quantitatively by gas chromatography and volumetry. Finally, the unreacted organometallic complex was removed by treatment under vacuum (10^{-4} Pa) at room temperature and then at 323 K for 10 h. The resulted solid was characterized by FTIR, ^{29}Si, ^{13}C, ^{27}Al and ^{119}Sn MAS NMR spectra, XRD, and elemental analysis.

The infrared spectrum of the HY zeolite before the reaction shows, in the ν(O–H) range, three bands at 3740 (weak), 3640 (strong) and 3545 (strong) cm^{-1} (Figure 1-a), which correspond respectively to silanols on the external surface, hydroxy groups in the supercage and hydroxy groups in sodalite cages or hexagonal prisms.[7] The relative proportions of these three types of hydroxy groups, determined by comparing the intensities of the bands (and assuming that the extinction coefficients are the same) are 3, 33 and 64%, respectively. This corresponds to 1.9 hydroxy groups in each supercage and 3.3 in the prisms and sodalite cages.

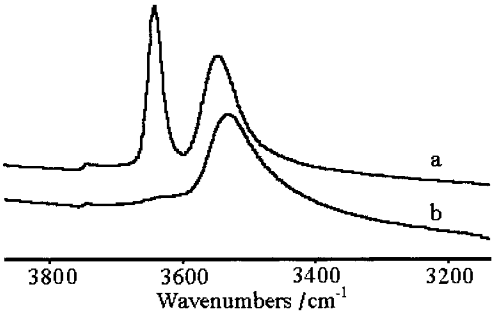


Figure 1. Infrared spectra, in the ν(O-H) range, of (a) HY zeolite, (b) HY zeolite contacted with tetramethyl tin during 1 h at room temperature.

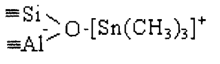
When tetramethyltin is introduced onto the HY zeolite at room temperature, gases evolve immediately. Both infrared spectroscopy and gas phase chromatography show that only methane is present in the gas phase. The most interesting feature is that after some minutes the amount of methane remains constant, showing that the reaction is very rapid at this temperature. Study as a function of the reaction temperature shows that the reaction occurs even at 190 K.

Infrared spectroscopy shows that the reaction occurs with the hydroxy groups of the zeolite (Figure 1-b): the evolution of methane is accompanied by a nearly complete consumption of the hydroxy groups in the supercage, a slight decrease (ca. 15%) of the hydroxy groups in the sodalite cages and/or prisms (the band is slightly shifted, probably due to the modification of the electronic density in the supercages), and no variation of the silanols, as expected from the studies on silica.[2] Simultaneously, ν(C–H) and ν(C–H) bands appear at 2900–3100 and 1200–1400 cm^{-1}, respectively. It should also be pointed out that ^{27}Al, ^{29}Si NMR and XRD data do not indicate any variation of the zeolite during and after the reaction with tetramethyltin, showing that the framework has retained its integrity.

Quantitative analysis of the evolved methane (2.3 mmol per g of HY zeolite) is in quite good agreement with the amount of consumed protons as deduced from the IR measurements (2.2 mmol per g of HY zeolite). All methane arises then from the reaction of tetramethyltin with protons of the HY zeolite. This result is also confirmed by the absence of methane evolution until 423 K when tetramethyltin is contacted with the NaY zeolite and the formation of monodeuterated methane when the HY zeolite has been preliminary deuterated. Chemical analysis of the sample after elimination of the physisorbed species gives a C/Sn ratio of 3.0 for the grafted organometallic complex (Sn% = 17–18 wt%, C% = 5.0–5.5 wt%), in agreement with the –Sn$(CH_3)_3$ formula.

^{13}C CP-MAS NMR gives only a sharp peak at +1.7 ppm. This value is slightly deshielded compared to those obtained on silica (–7.9 ppm) and even on cloverite. Similarly, ^{119}Sn is deshielded compared to its value in cloverite or on silica (Table1). These values are probably related to a more ionic character of the Sn–O bond in Y zeolite, leading to a positively charged tin fragment and then to increasing chemical shifts, the ^{119}Sn chemical shift of $[Sn(CH_3)_3]^+$ being +380 ppm .[8]

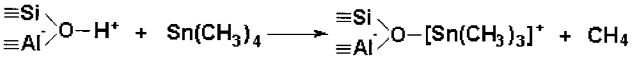
Table 1. ^{13}C and ^{119}Sn NMR chemical shifts of $Sn(CH_3)_4$ and –$Sn(CH_3)_3$ grafted on various supports

Tin species	Support	%Sn / wt	(^{13}C) δ/ppm	(^{119}Sn) δ/ppm	Ref.
$Sn(CH_3)_4$	neat		-9.6	0.0	2
≡Si-O-$Sn(CH_3)_3$	silica	2.23	-7.9	+136	2
≡T-O-$Sn(CH_3)_3$ T = P, Ga	cloverite	14.8	-3.4	+180	4
 $\genfrac{}{}{0pt}{}{\equiv Si}{\equiv Al^-}\rangle O\text{-}[Sn(CH_3)_3]^+$	HY	17.0	+1.7	+250	This work
$[Sn(CH_3)_3]^+ \bullet [AlCl_4]^-$	solution			+380	8

Another proof of the ionic character of the Sn–O bond in Y zeolite can be shown by infrared spectroscopy. Indeed, while the –O–$Sn(CH_3)_3$ fragment grafted onto silica gives, in the ν(C–H) domain, two bands with nearly the same intensities, on Y zeolite the band corresponding to the symmetric mode has a very weak intensity. This can be explained by assuming the above structure. Indeed, the polarization of the Sn–O bond will result in an increase of the Sn–O distance and then in an increase of the C–Sn–C angles, the –$Sn(CH_3)_3$ fragment becoming more planar. As a result, the variation of the dipolar momentum in the symmetric mode will decrease, resulting in a smaller intensity.

Kinetic studies from 192 to 243 K show that the methane evolution is proportional to the square root of time, as expected for a diffusion-limited reaction. The activation energy of the reaction (12 kJ/mol) is in agreement with this assumption. As methane will diffuse very rapidly through the pores of the zeolite, even after the grafting reaction, we can reasonably assume that the limiting step of the reaction is the diffusion of tetramethyltin through the pores, while the reaction with the hydroxy groups is very rapid.

These results show that tetramethyltin reacts with the hydroxy groups in Y zeolite as on the other supports, according to:



$$\genfrac{}{}{0pt}{}{\equiv Si}{\equiv Al^-}\rangle O{-}H^+ + Sn(CH_3)_4 \longrightarrow \genfrac{}{}{0pt}{}{\equiv Si}{\equiv Al^-}\rangle O{-}[Sn(CH_3)_3]^+ + CH_4$$

However, some differences can be pointed out: (i) only the hydroxy groups in the supercages react; (ii) the reaction occurs at very low temperature, showing that the acidity of the solid is a key parameter for its reactivity with such organometallic complexes; and (iii) that the resulting grafted organometallic fragment has a more ionic character than on silica or mordenite. Thus, the resulted material should have special properties as adsorbent or catalyst, due to the ionic characteristics of the –$Sn(CH_3)_3$ fragment. Preliminary results on the adsorption of hydrocarbons on this material show that the adsorption mechanism is completely different on unmodified (interaction with hydroxy groups) and on modified Y zeolite (interaction with the methyl groups of the organometallic fragment). As a result, the adsorption to benzene is stronger on modified HY than on HY.

References

1 J. Corker, F. Lefebvre, C. Lécuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, and J. M. Basset, *Science,* **271**, 966 (1996).

2 C. Nédez, A. Théolier, F. Lefebvre, A. Choplin, J. M. Basset, and J. F. Joly, *J. Am. Chem. Soc.*, **115**, 722 (1993).

3 C. Nédez, A. Théolier, F. Lefebvre, A. Choplin, J. M. Basset, J. F. Joly, and E. Benazzi, *Microporous Mater.*, **2**, 251 (1994).

4 M. Adachi, F. Lefebvre, C. Schott-Darie, H. Kessler, and J. M. Basset, *Appl. Surf. Sci.,* **121/122**, 355 (1997).

5 M. Adachi, F. Lefebvre, and J. M. Basset, *Chem. Lett.*, 1996, 221.

6 F. Lefebvre, J. P. Candy, A. de Mallmann, V. Dufaud, G. Niccolai, C. Santini, J. Thivolle-Cazat, and J. M. Basset, *L'Act. Chim. (Ec)*, **7**, 47 (1996).

7 P. A. Jacobs and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1,* **69**, 359 (1973).

8 J. J Eisch, K. Mackenzie, H. Windisch, and C. Krueger, *Eur. J. Inorg. Chem.*, **1**, 153 (1999).