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Pt(0)-Based Catalyst Supported on Silica Containing Di(ethylene oxide) Units for Hydrosilylation of Unsaturated Carbon−Carbon Bonds

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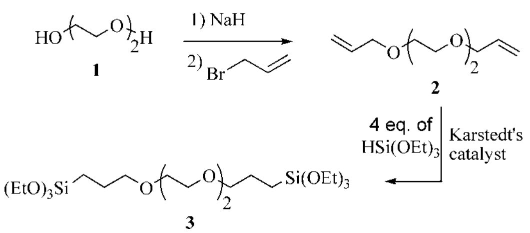
Hydrosilylation of unsaturated carbon−carbon bonds leading to C−Si bond formation is a widely used reaction on both the industrial and laboratory scale. Two platinum catalysts are mostly used to achieve this transformation: H_2PtCl_6, known as Speir's catalyst[1] and more recently a Pt(0) derivative, the Karstedt's catalyst[2] $(Pt_2\{(\eta^2\text{-viSiMe}_2)_2O\}_3$ where vi = vinyl), which is often preferred over the former, owing to its higher activity. Following the discovery of the Karstedt's catalyst, other modified platinum(0) complexes have also been described.[3,4]

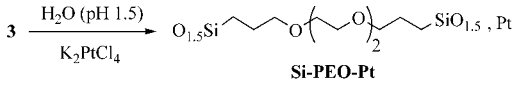
Although both hydrosilylation catalysts mentioned above are very efficient, they suffer from drawbacks of homogeneous transition-metal-based catalysts in the sense that they cannot be recovered and reused. Furthermore, to obtain metal-free products, which is highly desirable for products of pharmaceutical interest, their use requires laborious and time-consuming purification steps such as chromatography, distillation, or crystallization.

While immobilization of soluble transition-metal complexes on solid supports has given rise to much attention,[5,6] only few cases dealing with supported Pt catalyst for hydrosilylation have been reported.[7–11]

Scheme 1. Preparation of Bis(triethoxysilylpropyl)di(ethylene oxide) 3



Scheme 2. Preparation of the Material Si-PEO-Pt



Hybrid organic–inorganic materials prepared from molecular precursors containing at least two hydrolyzable $Si(OR)_3$ groups constitutes an expanding class of materials due to their potential applications in catalysis, adsorption, and separation, for example.[12] In the course of our investigations in this field, we found an original and efficient route to an immobilized platinum catalyst for hydrosilylation of unsaturated carbon−carbon bonds. In this contribution, we describe the preparation of an active, air-stable, recoverable, and reusable catalyst supported on silica containing di(ethylene oxide) units. The generation of the catalyst is based on the hydrolysis and polycondensation of α,*ω*-bis(triethoxysilylpropyl)di(ethylene oxide) in the presence of K_2PtCl_4 as the platinum source.

The precursor bis(triethoxysilylpropyl)di(ethylene oxide) **3** (Scheme 1) was prepared in two steps. Upon treatment of bis(ethyleneglycol) **1** by allyl bromide in the presence of NaH, the compound **2** was obtained in 92% yield. Hydrosilylation of the latter with $HSi(OEt)_3$ in the presence of the Karstedt's catalyst afforded, after distillation, the compound **3** in 89% yield. The latter was fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies as well as by elemental analysis. (The ^{1}H, ^{13}C, and ^{29}Si NMR spectra are given in Supporting Information.)

We observed that at pH = 1.5, the addition of **3** (1.03 g, 2 mmol) to a reddish aqueous solution (10 mL) of K_2PtCl_4 (0.415 g, 1 mmol) gave rise progressively to the formation of a black solid while the filtrate turned more and more pale and became perfectly colorless after 5 days at room temperature or 20 h at 60 °C. The recovered solid was copiously washed with H_2O, acetone, and ethanol to eliminate adsorbed K_2PtCl_4 and dried at 120 °C for 15 h affording a black solid named Si-PEO-Pt in 95% yield (Scheme 2).

Elemental analyses of Si-PEO-Pt revealed that the platinum, silicon, and carbon contents in this solid were 22.90,

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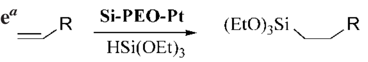
Table 1. Hydrosilylation of Unsaturated Carbon−Carbon Bonds by Triethoxysilane[a]



substrate	equiv $HSi(OEt)_3$	*T* (°C)	*T* (h)	yield[b] (%)
$CH_2{=}CH{-}(CH_2)_2Br$	5	60	36	95
$CH_2{=}CH{-}(CH_2)_3Br$	5	60	30	95
$CH_2{=}CH{-}(CH_2)_9Br$	5	50	36	94
$CH_2{=}CH{-}(CH_2)_7{-}COOCH_2CH_3$	1.5	80	40	95
$CH_2{=}CH{-}CH_2{-}O{-}(CH_2{-}CH_2{-}O)_2{-}CH_2{-}CH{=}CH_2$	4	80	36	90

[a] Using 2 mol % of Pt. [b] Isolated yield.

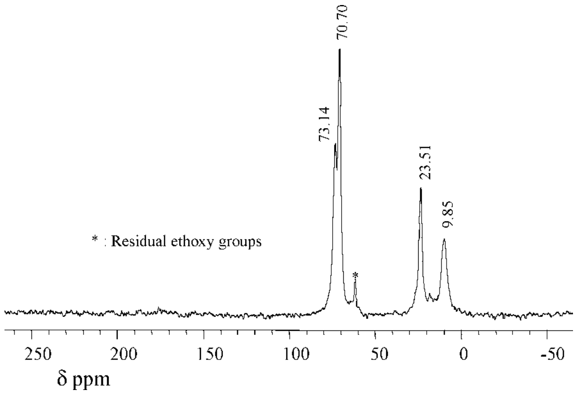


Figure 1. ^{13}C CP-MAS NMR spectrum of Si-PEO-Pt.

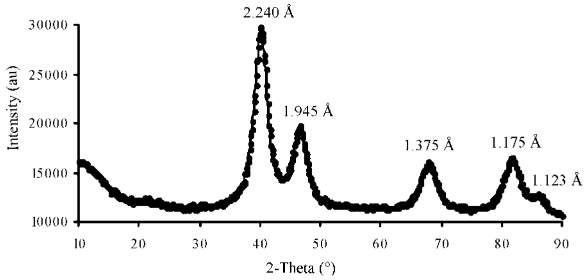


Figure 2. Powder XRD pattern of Si-PEO-Pt.

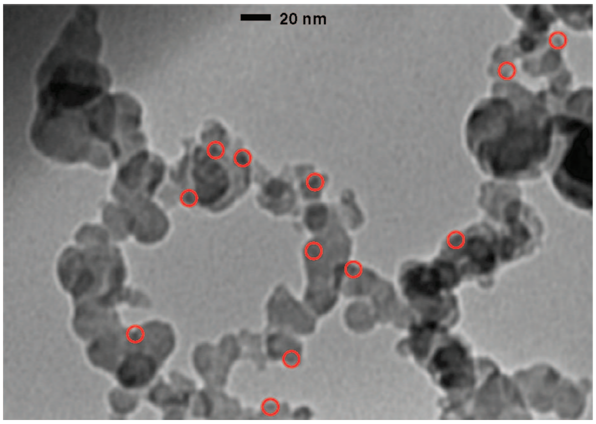


Figure 3. TEM image of Si-PEO-Pt.

14.14, and 33.92 wt %, respectively. The Si/Pt ratio was found to be 4.2, which is close to the expected value (4.0) when taking into account the initial ratio between **3** and K_2PtCl_4. The found Si/C ratio was 0.18 which is close to the theoretical value (0.2). The nitrogen adsorption measurement of Si-PEO-Pt was characteristic of a nonporous solid with a low surface area ($S_{BET} < 10\ m^2\ g^{-1}$). The ^{29}Si CP-MAS NMR spectrum of Si-PEO-Pt displayed a major signal at –66.41 ppm attributed to the T^3 [C-Si(OSi)$_3$] substructure, indicating that the solid Si-PEO-Pt is highly condensed. Two additional weak peaks at –109.74 and –100.35 ppm were attributed to Q^4 and Q^3 substructures probably originating from the hydrolysis and polycondensation of some residual $HSi(OEt)_3$ in the starting material (see Supporting Information) rather than a partial cleavage of Si-C bonds during the sol–gel process. The ^{13}C CP-MAS NMR spectrum of Si-PEO-Pt (Figure 1) revealed the presence of four signals at 9.85, 23.51, 70.70, and 73.14 ppm indicating the incorporation of the di(ethylene oxide) units.

The powder X-ray diffraction (XRD) pattern of Si-PEO-Pt within the range $2\theta = 30–90°$ (Figure 2) exhibits five pronounced diffraction peaks at $2\theta = 40.22°$, 46.77°, 68.41°, 81.98°, and 86.54° characteristic of crystalline Pt(0) with a face centered cubic (fcc) lattice.[13] On the basis of the Scherrer formula,[14] the average size of Pt(0) deduced from the XRD profile of Si-PEO-Pt was found to be 3.2 nm.

The presence of platinum metal nanoparticles in the hybrid material was confirmed by transmission electron microscopy (TEM). The TEM image of Si-PEO-Pt (Figure 3) shows clearly the formation of Pt(0) nanoparticles sized around 3–4 nm, coinciding with these determined from XRD pattern. It is worth noting that there is a low number of aggregated nanoparticles in the hybrid material.

Si-PEO-Pt was used as catalyst for addition of triethoxysilane to organic compounds containing unsaturated carbon−carbon bonds. The hydrosilylation reactions were carried out in a Schlenk tube under nitrogen atmosphere. The results are reported in Table 1.

It was found that hydrosilylation with $HSi(OEt)_3$ catalyzed by the Pt(0) nanoparticles into Si-PEO-Pt afforded the terminally silylated product in high yield without any purification. Gas chromatography analysis of the crude products revealed the formation of only one isomer. The ^1H NMR spectrum of the crude product resulting of the hydrosilylation of 11-bromo-1-undecene is given as an example in Supporting Information. The catalyst was recovered quantitatively by simple filtration and reused five times without leaching of Pt and any appreciable loss of the catalytic activity (Table 2).

It is worth noting that K_2PtCl_4 was the only platinum source able to give rise to an hydrosilylation catalyst by using **3**. Hydrolytic polycondensation of **3** in the presence of $PtCl_2$, H_2PtCl_6, or K_2PtCl_6 led to a colorless material, which appeared to be inactive toward hydrosilylation. Elemental

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(13) Powder Diffraction File, The International Centre for Diffraction Data.

(14) Scherrer formula: $d = k\lambda/\beta_{1/2} \cos\theta$, where k is the coefficient taken as 0.9, λ is the wavelength of X-ray radiation, and $\beta_{1/2}$ is the full-width at half maximum line width in radians.

Table 2. Hydrosilylation of 11-Bromo-1-undecene by 5 Equiv of $HSi(OEt)_3$ with Catalyst Recycling[a]

run	yield[b] (%)	run	yield[b] (%)
1	94	4	95
2	95	5	95
3	93		

[a] Reaction conditions: 2.7 molar % of Pt, 36 h at 50 °C. [b] Determined by ^1H NMR.

analysis of the resulting material revealed that the content in Pt was rather low (less than 0.5%), which should probably correspond to physical adsorption of the metal.

In addition, hydrolysis and polycondensation of α,ω-bis(trimethoxysilyl)octane in the presence of K_2PtCl_4 and under the same experimental conditions as for **3** gave rise to a colorless material, again inactive toward hydrosilylation. This result indicates the key role of diethylene oxide units toward the incorporation of K_2PtCl_4 into the hybrid material. Interestingly, the catalyst is stable in air and was conserved in an open flask without any loss of activity. In terms of practical applications, this is an important issue. Its stability toward air is probably due to the well encapsulation of the platinum nanoparticles within the hybrid material.

In conclusion, we have prepared a new platinum catalyst–supported on silica bearing di(ethylene oxide) units. This catalyst is active for hydrosilylation of unsaturated carbon−carbon bonds. The reactions proceed in high yields, and the catalyst may be recovered almost quantitatively by simple filtration and reused several times without leaching of platinum and loss of activity. On the basis of this recovery process, one can obtain metal-free compounds. This last feature combined with the air stability of the catalyst may be of interest for industrial applications, in particular for pharmaceutical products.

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Supporting Information Available: ^1H NMR, ^{13}C NMR, and ^{29}Si NMR of **3**, ^{29}Si CP-MAS NMR of Si-PEO-Pt, and ^1H NMR spectrum of the crude product (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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