

Pt nanoparticles immobilized in mesoporous silica: a non-leaching catalyst for 1-octene hydrosilylation

Supporting Information

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Platinum concentrations are expressed in ppm (microgram of platinum per gram of reaction mixture).

Turnover numbers (TONs) are defined as $\text{TON} = \frac{n_{\text{SiH}} \times \text{conversion}_{\text{SiH}}}{n_{\text{total Pt}}}$, with $\text{conversion}_{\text{SiH}}$ in the range [0-1].

S.1 Chemicals

Dibenzylideneacetone (dba), potassium tetrachloroplatinate (K_2PtCl_4) and 1-octene were bought from Sigma-Aldrich. The polymethylhydrosiloxane (PMHS) containing approximately 50 SiH units was generously provided by Bluestar Silicones France SAS. CDCl_3 was bought from Alfa Aesar. $\text{Pt}(\text{dba})_2$ was prepared using a literature procedure.¹ All products were used as received, except THF which was freshly distilled on Na/Benzophenone.

S.2 Hydrophilic Pt colloid preparation

This procedure has been reported by our group.²

100 mg (0.15 mmol) of $\text{Pt}(\text{dba})_2$ (dba = dibenzylideneacetone) and 90 mL of THF were introduced in a Fischer-Porter glass reactor under Ar, giving a deep purple solution. A solution of 25 mg of 3-chloropropylsilane (0.23 mmol, 1.5 eq) in 10 mL of THF was prepared under Ar and introduced in the Fischer-Porter reactor, which was then evacuated, pressurized at 3 bar of H_2 under stirring during 12 hours. A deep brown colloid was obtained, and stored under Ar.

S.3 Hydrophobic Pt colloid preparation

This procedure has been reported by our group.³

Same procedure as for hydrophilic Pt, replacing 3-chloropropylsilane by *n*-octylsilane.

S.4 Pt@{walls}SBA-15 (0.3% Pt w/w) preparation

This procedure has been reported by our group.²

In a 150 mL erlenmeyer, 0.5 g (86 μmol) of Pluronic®123, 50 mL of distilled water and 20 mg of NaF were vigorously stirred during 1 h. 20 mL of hydrophilic Pt colloid was then added, and the mixture was stirred 2 h more. The THF was then fully evaporated under reduced pressure.

In another erlenmeyer, 5 mL of water, 170 mg of HCl 37% w/w and 5 g (24 mmol) of tetraethylorthosilicate were stirred at 35 °C during 3 h.

The contents of both erlenmeyer were mixed together at 35 °C during 48 h. The grey solid was filtered, then washed with 2 × 20 mL of water, 2 × 20 mL of ethanol and 2 × 20 mL of diethyl ether. The solid was calcined under a flow of dry air (40 mL min^{-1}) at 350 °C during 10 h, with a ramp of 2 °C min^{-1} .

S.5 Pt@{pores}SBA-15 (0.3% Pt w/w) preparation

This procedure has been reported by our group.³

In a 150 mL erlenmeyer, 2.5 g (430 μmol) of Pluronic®123, 93 mL of distilled water and 290 mg of HCl 37% w/w were vigorously stirred during 1 h. 20 mL of a Pt colloid was then added, and the mixture was stirred 2 h more. The THF was then fully evaporated under reduced pressure. The mixture was then heated to 45 °C and 43 mg of NaF were added. The mixture was stirred during 48 h.

The grey solid was then filtered, then washed with 2×20 mL of water, 2×20 mL of ethanol and 2×20 mL of diethyl ether. The solid was calcined under a flow of dry air (40 mL min^{-1}) at 350 °C during 10 h, with a ramp of 2 °C min^{-1} .

S.6 Pt/SiO₂ (0.3% Pt w/w) preparation

3 g of fumed silica were impregnated (Incipient Wetness Impregnation) with 30.7 mL of hydrophobic Pt colloid that was concentrated to 4.5 mL under reduced pressure.

The solid was calcined under a flow of dry air (40 mL min^{-1}) at 350 °C during 10 h, with a ramp of 2 °C min^{-1} .

S.7 Transmission electron microscopy

Transmission Electron Microscopy (TEM) of the Pt@{walls}SBA-15 solid was performed at the “Centre Technologique des Microstructures”, Université Lyon 1, Villeurbanne, France, with a JEOL2100F transmission electron microscope, using an acceleration voltage of 200 kV. The samples were prepared with copper grids covered with an amorphous carbon film.

S.8 Catalytic tests

Warning : the hydrosilylation reaction is very exothermic! The reaction medium temperature must be monitored carefully to prevent a runaway.

Blank tests were performed at several points of the study and indicated that the reactor was not contaminated by traces of catalysts.

The hydrosilylation catalysts were found to be very sensitive to the grade of the octene used. When using octene of industrial grade, conversions significantly lower were obtained, and the presence of traces of poisons in the octene were suspected to be at the origin of these lower performances.

The catalytic tests were run under an atmosphere of air, in a classic 300 mL glass reactor equipped with a glass impeller and baffles. The stirring rate was 1000 rpm. At the beginning

of the reaction, the reactor was filled with 43 g of 1-octene (1.4 equivalent respective to SiH, to compensate for alkene isomerization) and 114 mg of Pt@{walls}SBA-15(6 ppm Pt).

The 1-octene/catalyst mixture was heated to 75 °C. Then, 17 g of PMHS were added at 0.3 mL min⁻¹ with a syringe pump. The temperature of the reaction medium was maintained between 75 °C and 85 °C by removing partly or totally the heating bath. After the end of the PMHS addition, samples were regularly collected, diluted in CDCl₃ and analysed by ¹H NMR to get the SiH conversion.

S.9 SiH conversion calculation method

This method has been reported by our group.⁴

An example of proton NMR spectrum of the reaction mixture of a catalytic test is given in Fig. S1.

The signal at 0.5 ppm corresponds to the CH₂Si of hydrosilylated SiH, the signal at 0.85 ppm corresponds to the CH₂CH₃ of all octyl chains and 2-ethyl-1-hexene, the signal at 4.7 ppm corresponds to the SiH protons plus 1-ethyl-2-hexene, an impurity contained in 1-octene, the signal at 5.3 ppm corresponds to both CH of 2-octene (formed in the medium by isomerization of 1-octene) and the signal at 5.7 ppm corresponds to the CH of 1-octene.

The quantity of 2-ethyl-1-hexene is

$$ethylhexene = \frac{I_{0.85ppm}/3 - I_{5.7ppm} - I_{5.3ppm}/2 - I_{0.5ppm}/2}{3}$$

The SiH conversion is

$$X_{SiH} = \frac{functionnalizedSiH}{functionnalizedSiH + unfunctionnalizedSiH}$$

hence

$$X_{SiH} = \frac{I_{0.5ppm}/2}{I_{0.5ppm}/2 + (I_{4.7ppm} - ethylhexene/2)}$$

References

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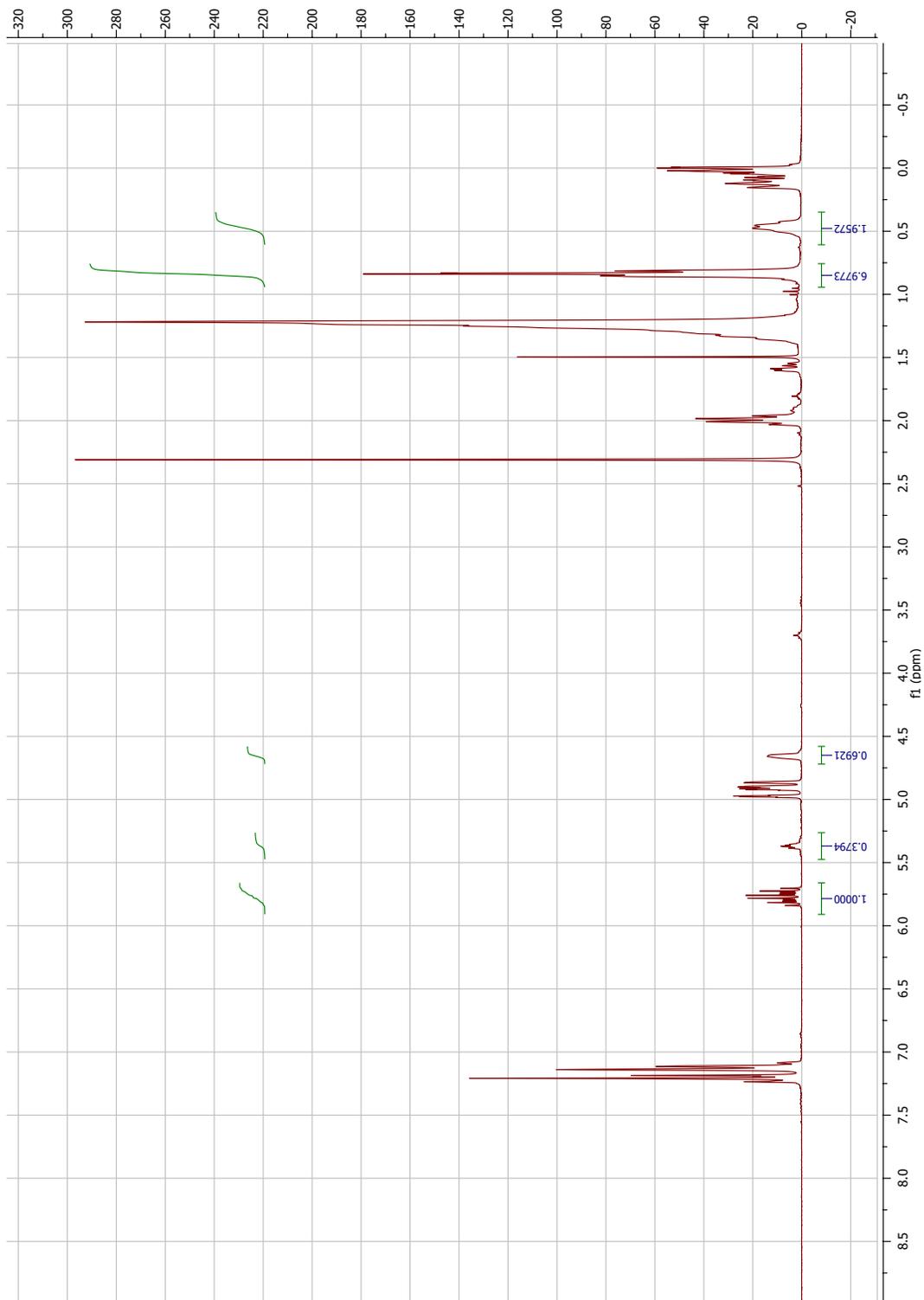


Fig. S1 Example proton NMR spectrum of the crude of a catalytic test.