

Platinum nanoparticles in suspension are as efficient as Karstedt's catalyst for alkene hydrosilylation

Supporting Information

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All experiments were run in duplicate. Platinum concentrations are expressed in ppm (microgram of platinum per gram of reaction mixture).

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 and Karstedt's catalyst (10% w/w Pt solution in a neutral silicone oil) were generously provided by Bluestar Silicones France SAS. *n*-octylsilane was bought from ABCR. $CDCl_3$ was bought from Alfa Aesar. Toluene was bought from Carlo Erba, dried in a MBraun SPS-800 system, and degassed using the freeze-pump-thaw method. $Pt(dba)_2$ was prepared using a literature procedure.¹

S.2 Preparation and characterization of the colloidal suspensions

General procedure : 43 mL of toluene and 0.015 mmol of the platinum precursor were introduced in a dry schlenk tube under argon. The solution was transferred into a dry Fisher-Porter vessel under argon using a canula. 1.5 equivalent of stabilizer was added. The solution was put under 4 bars of H_2 , and stirred at room temperature overnight. The resulting colloidal solutions contained 80 ppm of platinum.

Colloid1 : The general procedure was used, with $Pt(dba)_2$ (10 mg, 0,015 mmol) as platinum precursor and *n*-octylsilane (3.3 mg, 0,023 mmol) as stabilizer. This synthesis has already been published.²

Colloid2 : The general procedure was used, with Karstedt's catalyst (29.4 mg of a 10% solution, corresponding to 2.9 mg of platinum, 0.015 mmol of Pt) as platinum precursor and the PMHS (4.2 mg, 0.023 mmol) as stabilizer.

Colloid3 : The general procedure was used, with Karstedt's catalyst (29.4 mg of a 10% solution, corresponding to 2.9 mg of platinum, 0.015 mmol of Pt) as platinum precursor and *n*-octylsilane (3.3 mg, 0.023 mmol) as stabilizer.

S.2.1 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) of the platinum colloids 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 by depositing a drop of colloidal solution on a copper grid covered by a carbon film and letting it dry.

The micrographs and particle size distributions of the colloids are presented in Fig. S1.

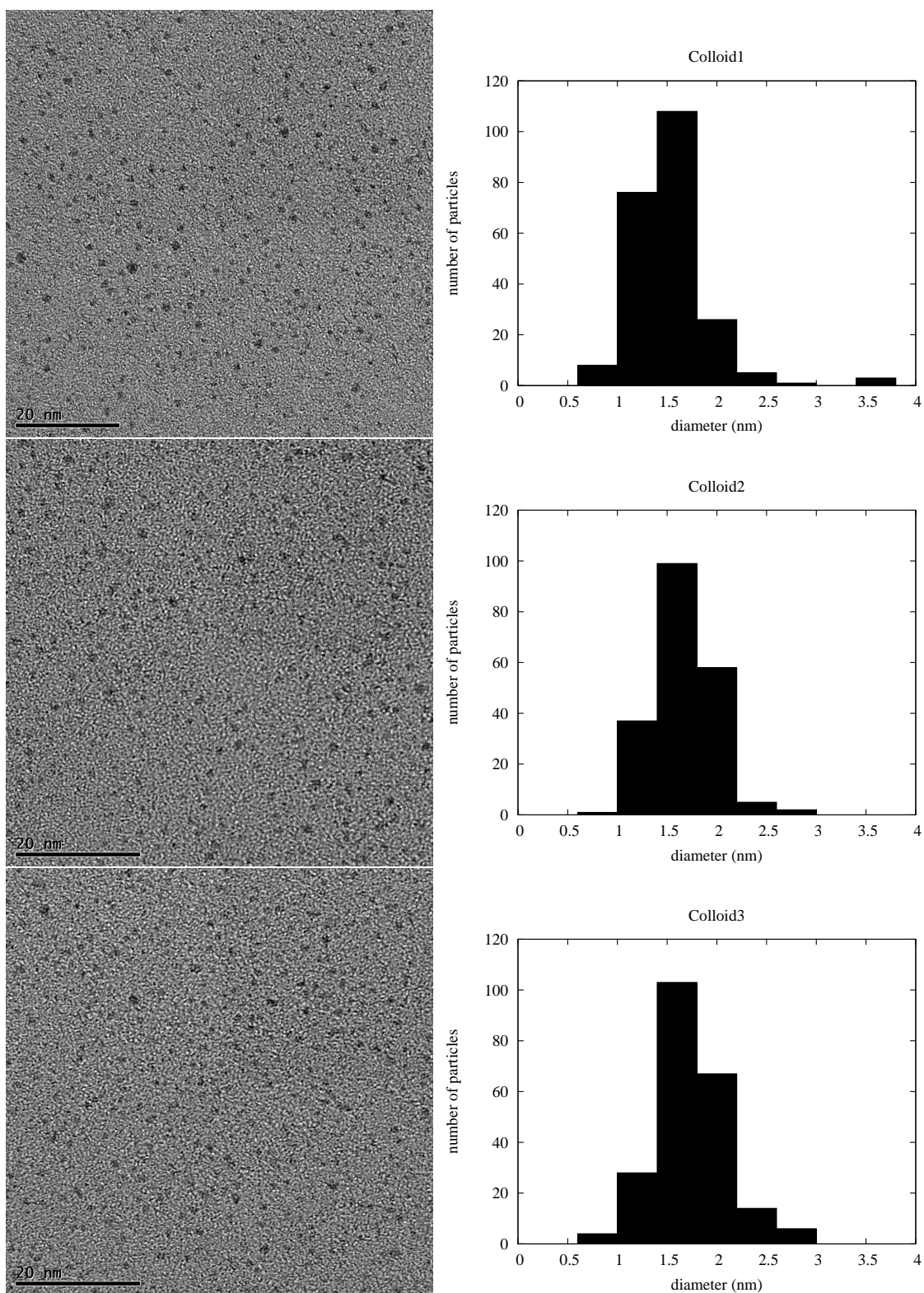


Fig. S1 Transmission Electron Micrograph and particle size distribution of the colloids. Top : Colloid1, Middle : Colloid2, Bottom : Colloid3.

S.2.2 Pt precursor decomposition

We assessed that the decomposition of the Pt(0) precursor was quantitative using UV/visible spectroscopy (see Fig. S2). Indeed, the spectrum of the colloidal solution shows the absence of the $\text{Pt}(\text{dba})_2$ absorption band, indicating a total conversion of the precursor.

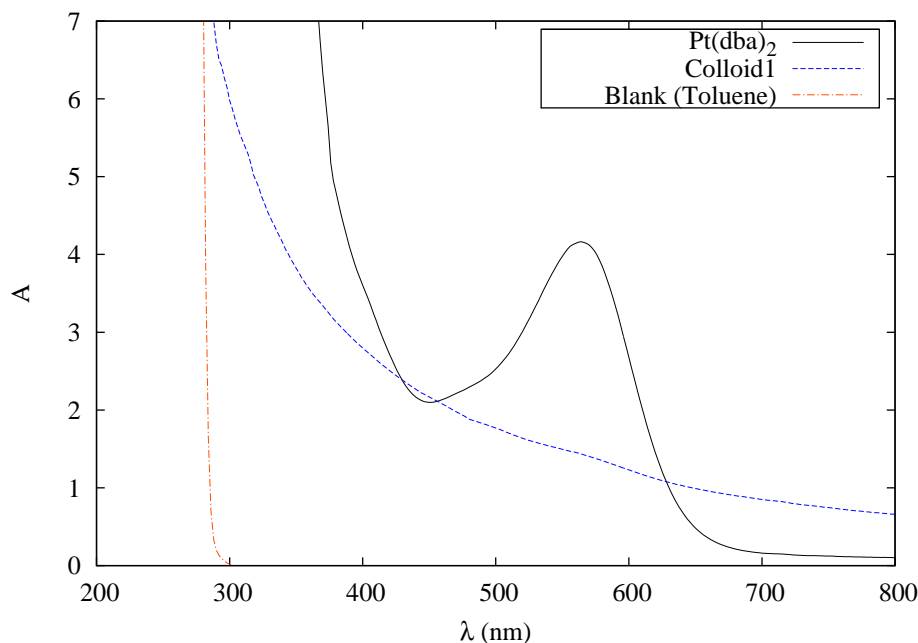


Fig. S2 UV/Visible spectra of Colloid1 and a $\text{Pt}(\text{dba})_2$ solution at same total platinum concentration.

We checked that a Celite® plug could selectively adsorb platinum nanoparticles but not platinum complexes such as $\text{Pt}(\text{dba})_2$ (see Fig. S3). Such solutions of platinum nanoparticles filtered on Celite® were not active in alkene hydrosilylation, while $\text{Pt}(\text{dba})_2$ solutions filtered on Celite® were active, proving that the catalytic activity of platinum nanoparticles was essentially heterogeneous.

S.3 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.



Fig. S3 Adsorption experiments of a solution of Pt nanoparticles (left) and $\text{Pt}(\text{dba})_2$ (right) on a Celite® plug.

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 relative to SiH, to compensate for alkene isomerization). For 7 ppm tests, 6 g (6.9 mL) of colloidal solution were added. For 0.5 ppm tests, 0.37 g (0.43 mL) of colloidal solution were added. When Karstedt's catalyst was used, it was diluted with toluene to reach the same Pt concentration in the reaction medium. The 1-octene/catalyst mixture was heated to 75°C. Then, 17 g of PMHS were added at 0.3 ml/min 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 CDCl_3 and analysed by ^1H NMR to get the SiH conversion.

We observed that when colloids were not perfectly dispersed (presence of some aggregates on the TEM), the SiH conversions were significantly lower. The presence of aggregates may indicate that the particles are not perfectly stabilized, for example because of a lack of silane stabilizer, and the particles may aggregate further when heated in the reaction medium, thus decreasing their activity.

S.4 Celite adsorption during reaction

We used Celite's ability to selectively adsorb Pt NPs but not Pt complexes such as $\text{Pt}(\text{dba})_2$ (see S.2.2) to probe the homogeneous/colloidal nature of the active species when using Pt NPs as precatalyst.

We performed a semi-batch experiment at 60°C with a short PMHS addition (2 g PMHS over 5 min in 42 g of 1-octene containing 7 ppm Pt under the form of Pt NPs), after which we took a sample of the reaction medium. We filtrated this sample on a celite plug (4 cm Celite in a glass pipette). The SiH conversion in the filtrate was 57%. The filtrate was put at 60°C during 1 h, after which the SiH conversion was 62%. In the same amount of time, the SiH conversion in the reactor had progressed to 80%. We concluded that when using Pt NPs catalytic activity was essentially due to the NPs themselves and not a dissolved Pt species.

S.5 SiH conversion calculation method

An example of proton NMR spectrum of the reaction mixture of a catalytic test is given in Fig. S4.

The signal at 0.5 ppm corresponds to the CH_2Si of hydrosilylated SiH, the signal at 0.85 ppm corresponds to the CH_2CH_3 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

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

The SiH conversion is

$$X_{\text{SiH}} = \frac{\text{functionalizedSiH}}{\text{functionalizedSiH} + \text{unfunctionalizedSiH}}$$

hence

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

References

- 1 K. Moseley and P. M. Maitlis, *J. Chem. Soc. D: Chem. Comm.*, 1971, 982–983.
- 2 M. Boualleg, J.-M. Basset, J.-P. Candy, P. Delichere, K. Pelzer, L. Veyre and C. Thieuleux, *Chem. Mater.*, 2009, **21**, 775–777.

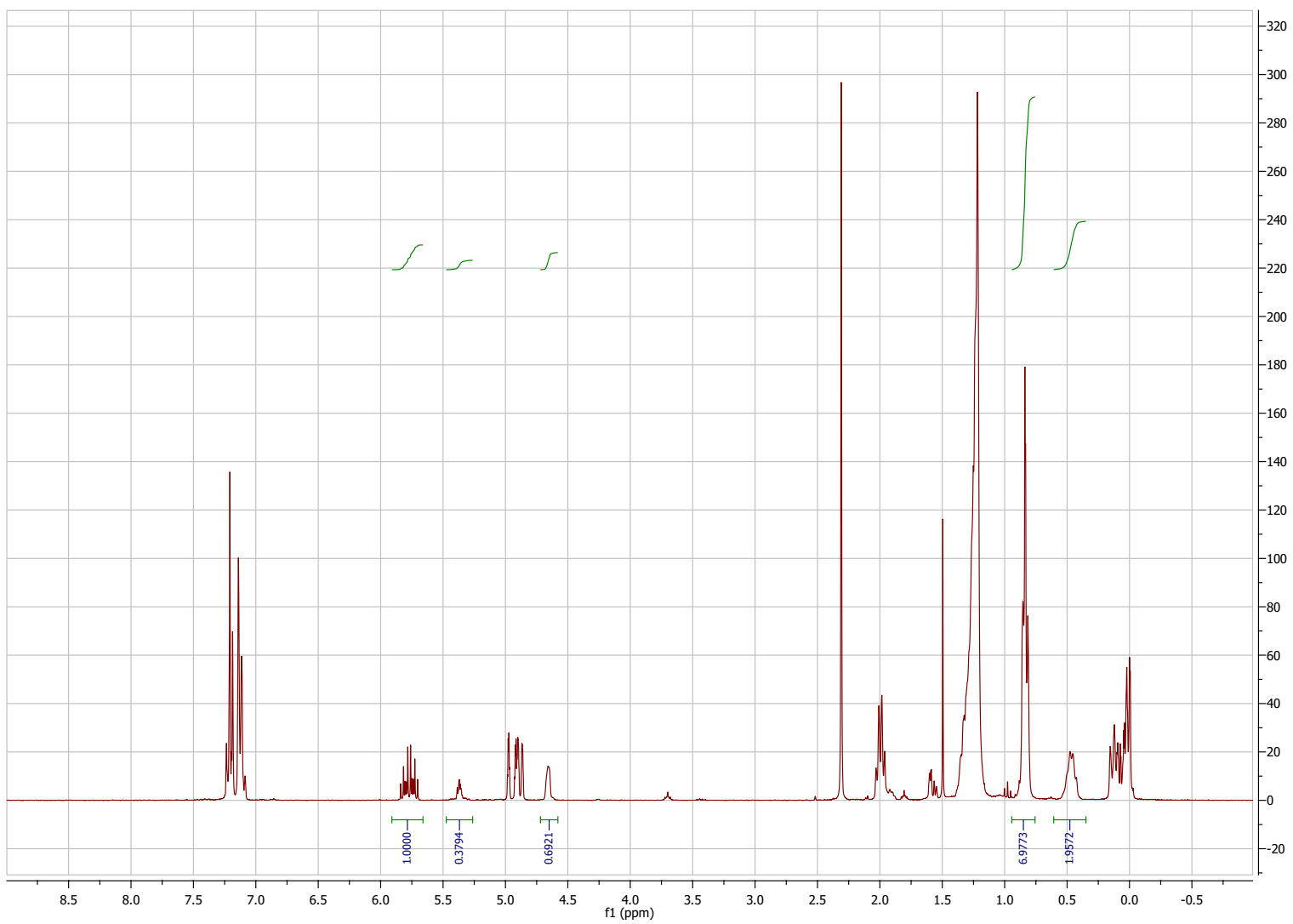


Fig. S4 Example proton NMR spectrum of the crude of a catalytic test.