

Supporting Information

New approach for the preparation of Rh and Pt nanoparticles stabilized by phosphine functionalized silica for selective hydrogenation reactions.

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S1. General conditions

All experiments were carried out under inert atmosphere, either N₂ or Ar. Schlenk and glove-box techniques were used for the synthesis of the organometallic compounds. For the synthesis and treatment of the modified silica materials, a high- vacuum line (about 1 Pa) and a glove box were used. Diethyl ether and pentane were distilled on Na/K- benzophenone and degassed through freeze- pump- thaw cycles. RhCl₃·xH₂O and Pt(dba)₃ were purchased from Sigma Aldrich Company. Elemental analysis was performed at the Mikroanalytisches Labor Pascher, Remagen (Germany). DRIFT spectra were recorded on a Nicolet 6700 FTIR by using airtight cells. Solid- state ¹H MAS ³¹P NMR and ¹³C CP/MAS-NMR spectra were recorded on a Bruker Avance 500 spectrometer with a conventional double- resonance 4mm CO-MAS probe at the Laboratoire de Chimie Organométallique de Surface of the Ecole Supérieure de Chimie Physique Electronique of Lyon. The samples were loaded under argon atmosphere into a zirconia rotor, which was then tightly closed. Chemical shifts are given with respect to TMS as an external reference for the ¹H, ¹³C and ³¹P NMR data.

S2. Synthesis and characterization of the supports

Preparation of SiO₂₋₇₀₀ :

Silica Aerosil (Degussa) with a specific area of 200 m²g⁻¹ was calcined at 500 °C for 4h then dehydroxylated at 700°C for 12h under a high vacuum (10⁻⁵ mmHg). The DRIFT spectrum features the characteristic isolated SiOH peak at 3747 cm⁻¹.

Preparation of [(≡SiO)₂Al*i*Bu.(Et₂O)]:

Using the double Schlenk technique, SiO₂₋₇₀₀ (3.9 g) was treated with 1.2 % excess [(Al*i*Bu₃) (Et₂O)] in diethylether (10 ml) for 2h at room temperature. After repeated washings with diethylether (10ml), followed by evacuation of the volatile under high vacuum (10⁻⁵ mmHg), the modified silica was afforded as a white powder and characterized by DRIFT, solid- state NMR spectroscopy and mass- balance analysis.

The DRIFT spectrum features the characteristic stretching bands of C-H bond around 2800-3000 cm⁻¹. Phase Gas analysis by GC: 0.87 *i*BuH/Al. Elemental analysis: % Al= 1.6, % C= 7.6, C/Al= 11.

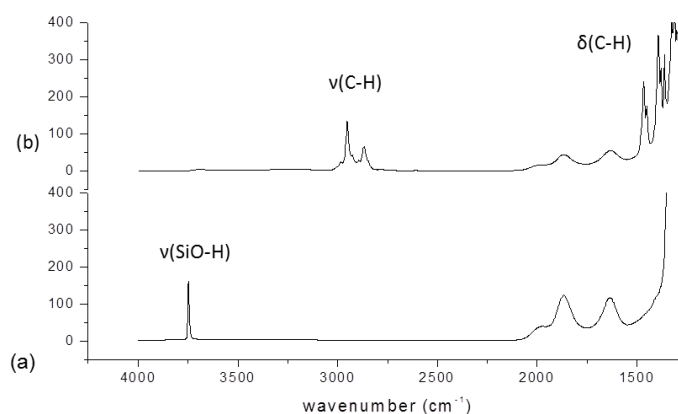


Figure 1 DRIFT spectroscopy of a) SiO₂₋₇₀₀ b) [(≡SiO)₂Al*i*Bu.(Et₂O)]

^1H solid-state NMR (500Hz, δ in ppm): -0.1 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 0.9 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$, $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 1.2 ($\text{O}(\text{CH}_2\text{CH}_3)_2$), 1.8 ($\text{MCH}_2\text{CH}(\text{CH}_3)_2$), 3.8 ($\text{O}(\text{CH}_2\text{CH}_3)_2$).

^{13}C CP-MAS solid-state NMR (500Hz, δ in ppm): 14 ($\text{O}(\text{CH}_2\text{CH}_3)_2$), 22 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$), 24-28 ($\text{AlCH}_2\text{CH}(\text{CH}_3)_2$, $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 65 ($\text{O}(\text{CH}_2\text{CH}_3)_2$).

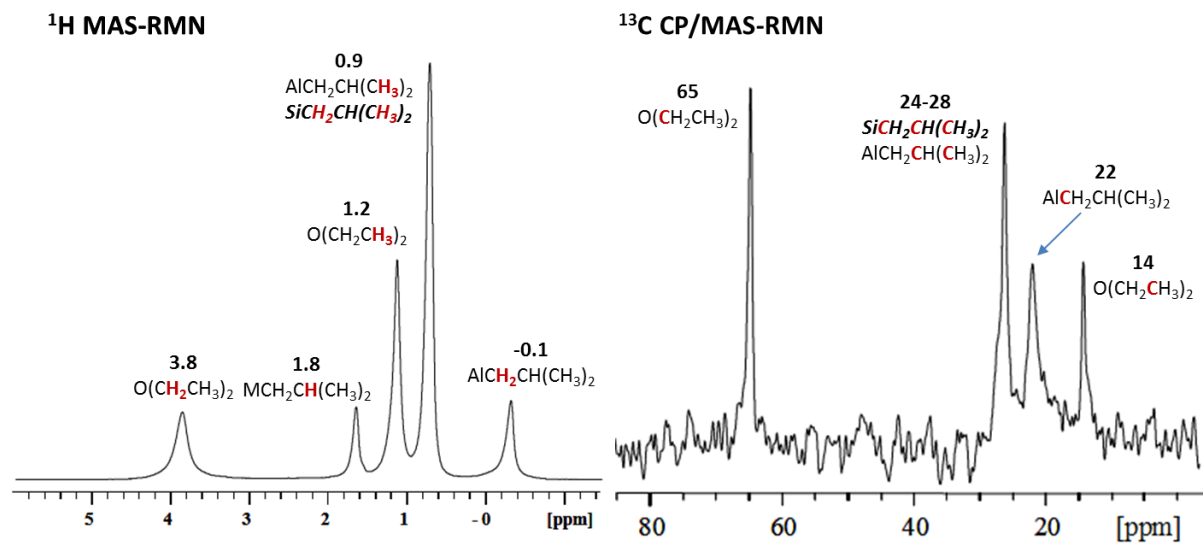


Figure 2 ^1H (left) and ^{13}C (right) NMR of the $[(\equiv\text{SiO})_2\text{AlBu} \cdot (\text{Et}_2\text{O})]$

Preparation of the phosphine modified silica P-SiO₂:

Using the double Schlenk technique, [(≡SiO)₂Al*i*Bu.(Et₂O)] (3 g) was treated with 1.2 % excess of 4-(diphenylphosphino)phenol (0.2296 g) in pentane (10 ml) for 2h at room temperature. After repeated washings with pentane (10 ml), followed by evacuation of the volatile under high vacuum (10⁻⁵ mmHg), the modified silica was afforded as a white powder.

The DRIFT spectrum features the characteristic stretching bands for C-H bond around 2800-3000 cm⁻¹, the stretching bands for C_{2p2}-H above 3000 cm⁻¹ and for C=C around 1700- 1800 cm⁻¹.

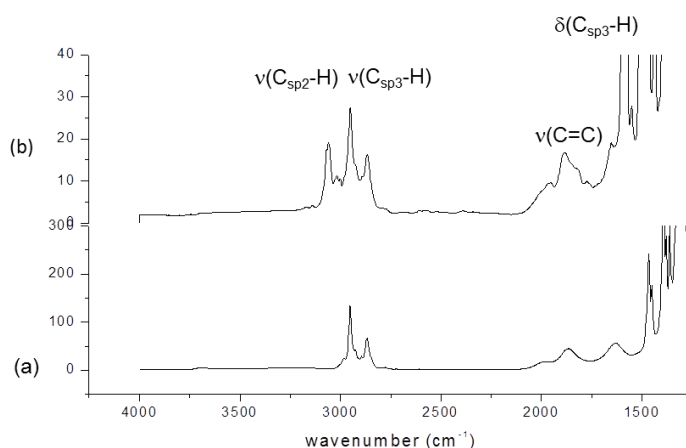


Figure 3 DRIFT spectroscopy of a) [(≡SiO)₂Al*i*Bu.(Et₂O)] b) P-SiO₂

Phase gas analysis by GC: 0.87 *i*BuH/Al.

¹H solid-state NMR (500Hz, δ in ppm): 0.8 (SiCH₂CH(CH₃)₂), 4.1 (O(CH₂CH₃)₂), 6.8 (Ar-H).

¹³C CP-MAS solid- state NMR (500Hz, δ in ppm): 12.69 (O(CH₂CH₃)₂), 25.69 (AlCH₂CH(CH₃)₂), 126.66-132.81 (Ar-C) .

³¹P CP-MAS solid-state NMR (500Hz, δ in ppm): (-6.18 P of P-SiO₂).

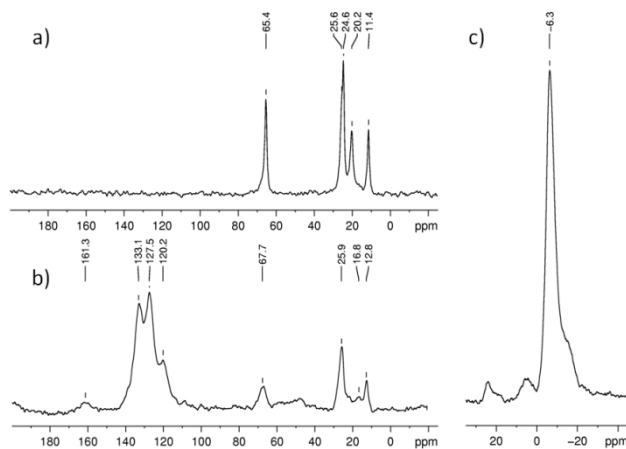


Figure 4 ¹³C CP MAS NMR spectra of [(≡SiO)₂Al*i*Bu.(Et₂O)] (a) and P-SiO₂ (b) (125.7 MHz, 30000 scans, relaxation delay of 2s, CP contact time of 2ms, 10 kHz spinning speed) and ³¹P CP MAS NMR spectrum of P-SiO₂ (c) (202.4 MHz, 6000 scans, relaxation delay of 2s, CP contact time of 2ms, 10 kHz spinning speed).

S3. Synthesis and characterization of the nanoparticles

Preparation of the rhodium precursor

The synthesis was carried out according to the procedure described in the literature.^{1,2} Allylmagnesium bromide (35 mmol) was added to a cold suspension (-10 °C) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.1 g, 5.3 mmol) in THF (93 ml). The solution slowly lost its red-brown color to become yellow. The solution was then allowed to warm to room temperature and stirred for an additional 16 hours at 0 °C. The solvent was removed under reduced pressure and the residue extracted with pentane (previously distilled and deoxygenated) (3x20mL). The sublimation was carried out in a water bath at 40 °C and of yellow crystals formed onto the cold finger were collected. (Yield= 520 mg, 55 %)

The purity of this complex was checked by ^1H and ^{13}C NMR spectroscopy.³

Preparation of the soluble rhodium nanoparticles Rh-NPs

The synthesis of the Rh nanoparticles was carried out following the method reported by Chaudret and co-workers.⁴ In a typical procedure, the $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3]$ (64 mg, 0,28 mmol) was placed into a Fischer-Porter reactor and dissolved at -110 °C (acetone/ N_2 bath) in 64 mL of dry and deoxygenated THF (using freeze-pump-thaw techniques) in the presence of 0.4 equivalents of the PPh_3 ligand. The Fischer-Porter reactor was then pressurized under 6 bar of H_2 and stirred for 30 minutes at room temperature. The solution was then heated to 40 °C and stirred at this temperature during 24h. The initial colorless solution became black after 1h. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15 ml) was then carried out, obtaining a black precipitate. (Yield= ca. 25-30 mg, 30-35 %)

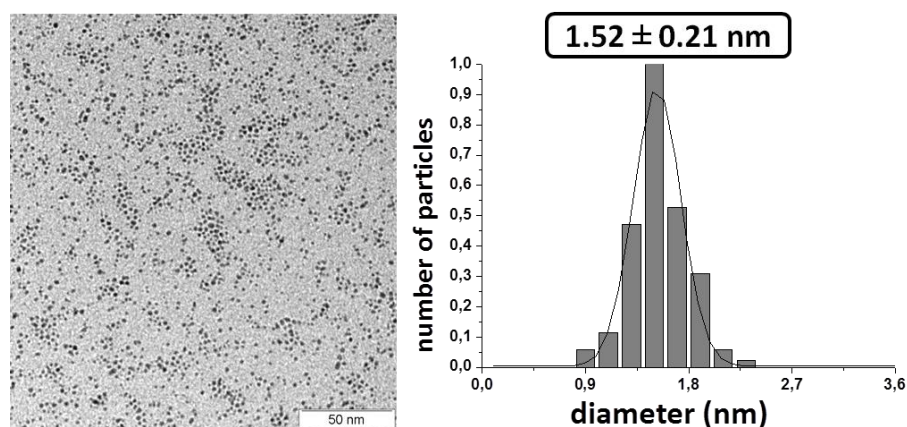


Figure 5 TEM micrograph and size distribution of the Rh- NPs

Preparation of the NPs@SiO₂ without extra phosphine as stabilizer.

0.125 g of P-SiO₂ was reacted with (50.34 mg) of Pt(dba)₃ in 50 ml of degassed THF for 12 h at 25°C under 3 bar of H₂. After evaporation of THF, the powder was washed three times with pentane. The resulting black powder was dried under vacuum and stored in the glove box.

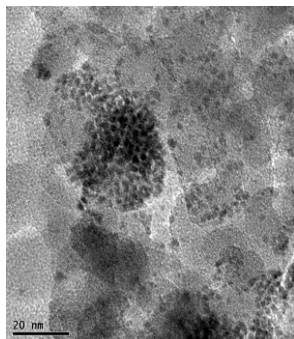


Figure 6: TEM Analysis of platinum nanoparticles grafted on silica ₇₀₀

The desired amount of the previously synthesized phosphine modified silica (250mg) and 29 mg of the [Rh(η^3 -(C₃H₅)₃)] were placed in 30 ml of dry and deoxygenated THF (using freeze-pump-thaw techniques). The Fischer-Porter reactor was then pressurized under 4 bar of H₂ and the solution was heated to 40°C overnight. The solution turned black after a few hours. A carbon-covered copper grid for transmission electron microscopy was prepared with a small amount (5 drops approx.) under argon atmosphere. The solution was concentrated under reduced pressure.

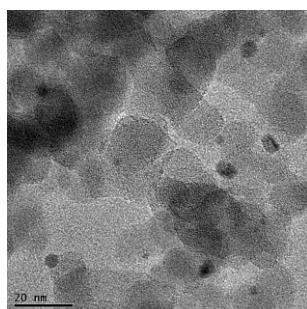


Figure 1: TEM Analysis of rhodium nanoparticles grafted on silica ₇₀₀

Preparation of the rhodium nanoparticles Rh-NPs@SiO₂ with extra phosphine as stabilizer.

The silica previously dehydroxylated at 700 °C (SiO₂₋₇₀₀) (500mg), 62,5 mg of the [Rh(η^3 -C₃H₅)₃] and 27,5 mg of triphenylphosphine, were placed in 60 ml of dry and deoxygenated THF (using freeze-pump-thaw techniques). The Fischer-Porter reactor was then pressurized under 4 bar of H₂ and the solution was heated to 40°C overnight. The solution turned black after a few hours. A carbon-covered copper grid for transmission electron microscopy was prepared with a small amount (5 drops approx.) under argon atmosphere. The solution was concentrated under reduced pressure. The black powder was characterized by:

TEM: Nanoparticles of 2.55 ± 0.42 nm of mean diameter.

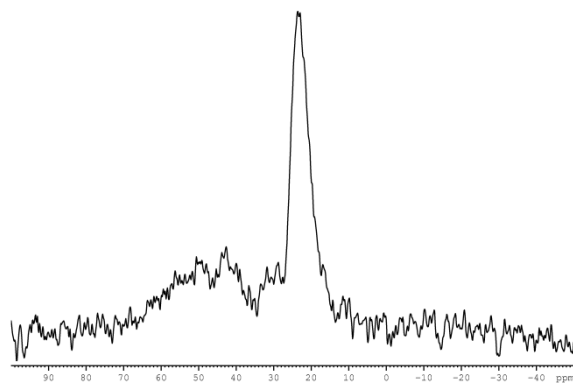


Figure 8 31 P SS NMR of Rh-NPs@SiO₂

Preparation of the platinum nanoparticles Pt-NPs@SiO₂ with extra phosphine as stabilizer.

400 mg of SiO₂-700 was reacted with (50.34 mg) of Pt(dba)₃ and 12 mg of PPh₃ (0.4 eq) in 100 ml of degassed THF for 12h at 25 °C under 3 bar of H₂. After evaporation of THF, the powder was washed three times with pentane. The resulting black powder was dried under vacuum and stored in the glove box .

TEM: Nanoparticles of 1.60 ± 0.40 nm of mean diameter.

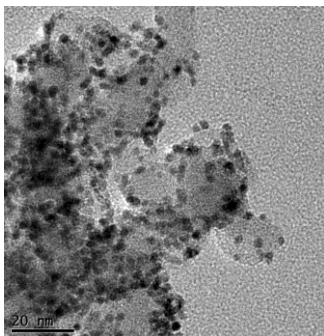


Figure 9: TEM Analysis of platinum nanoparticles Pt-NPs@SiO₂ grafted on silica₇₀₀ stabilized by PPh₃

Preparation of the rhodium nanoparticles Rh-NPs@P-SiO₂

The desired amount of the previously synthesized phosphine modified silica (500mg), 62,5 mg of the [Rh(η³-(C₃H₅)₃)] and 27,5 mg of triphenylphosphine, were placed in 60 ml of dry and deoxygenated THF (using freeze-pump-thaw techniques). The Fischer-Porter reactor was then pressurized under 4 bar of H₂ and the solution was heated to 40°C overnight. The solution turned black after a few hours. A carbon-covered copper grid for transmission electron microscopy was prepared with a small amount (5 drops approx.) under argon atmosphere. The solution was concentrated under reduced pressure. The black powder was characterized by:

Elemental analysis: % P: 1.27 % Rh: 4.36

TEM: Nanoparticles of 1.17 ± 0.18 nm of mean diameter, distributed only onto the support.

³¹P CP-MAS solid-state NMR (500Hz): δ (21, 26, 42 ppm).

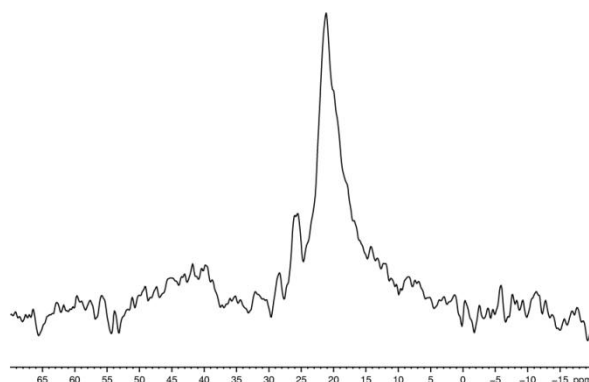


Figure 10 ³¹P SS NMR of Rh-NPs@P-SiO₂

Preparation of the platinum nanoparticles Pt-NPs@P-SiO₂

400 mg of P-SiO₂ was reacted with 50.34 mg of commercial from Sigma-Aldrich Pt(dba)₃ and 12 mg of PPh₃ (0.4 eq) in 100 ml of degassed THF for 12h at 25 °C under 3 bar of H₂. A small amount (5 drops approx.) of the solution was deposited under argon atmosphere on a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15 ml) was then carried out, obtaining a grey precipitate. The solution was dried over vacuum to obtain a crystalline black powder.

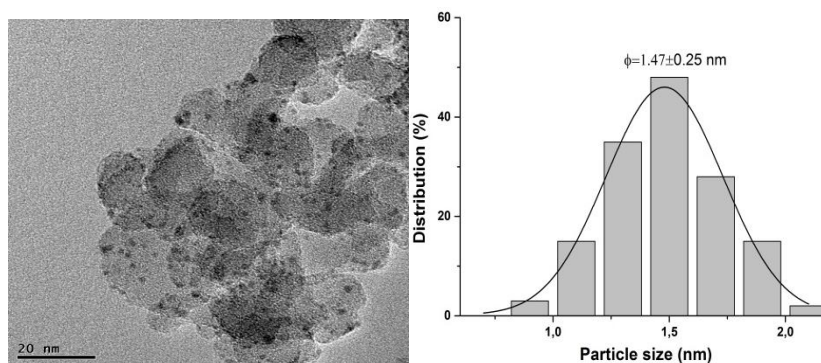


Figure 11 TEM micrograph and size distribution of platinum nanoparticles Pt-NPs@P-SiO₂.

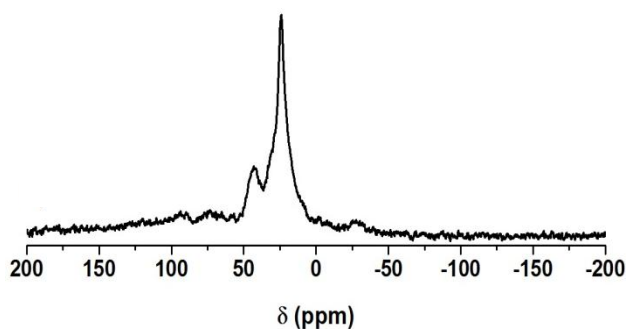


Figure 12 ³¹P SS NMR of Pt-NPs@P-SiO₂

S4. Catalytic tests

Hydrogenation reactions were performed by autoclave using heptane as a solvent for 4h under 40 bar at 80 °C. Aromatic products were analyzed in line by GC (HP 5890 chromatograph fitted with HP-5 30 m x 0.32 mm x 0.25µm capillary column, FID detector) and GC-MS (HP 6890 chromatograph / 59975C mass selective instrument fitted with HP-5 30 m x 0.25 mm x 0.25µm capillary column and chem station software).

¹ M. D. Fryzuk, W. E. Piers in *Organometallic Syntheses* (Eds.: R. B. King, J. J. Eisch), Elsevier, Amsterdam, **1986**, vol. 3, p.128.

² W. A. Herrmann in *Synthetic Methods of Organometallic and Inorganic Chemistry* (Ed.: W. A. Herrmann), Thieme, Stuttgart, **1996**, p. 38.

³ K. D. John, K. V. Salazar, B. L. Scott, R. T. Baker, A. P. Sattelberger, *Organometallics*, **2001**, *20*, 296-304.

⁴ J. García-Antón, M. R. Axet, S. Jansat, K. Philippot, B. Chaudret, T. Pery, G. Buntkowsky, H.-H. Limbach *Angew. Chem. Int. Ed.* **2008**, *47*, 2074-2078.