

Alkene hydrosilylation with supported and unsupported Ni nanoparticles: strong influence of the Ni environment on activity and selectivity

Supporting Information

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S.1 Chemicals

Toluene was bought from Carlo Erba, purified in a MBraun SPS-800 system, stored on activated 3 Å molecular sieves and degassed. C₆D₆ was bought from Euriso-top, stored on activated 3 Å molecular sieves and degassed. Ni(COD)₂ was bought from STREM chemicals and used as received. (EtO)₃SiH and (EtO)SiVi were bought from Alfa Aesar. Dodecane was bought from Sigma Aldrich. *n*-octylsilane was bought from ABCR. Fumed silica (Aerosil® 200) was bought from Evonik.

S.2 Catalysts synthesis

S.2.1 Ni₃Si₂ colloidal solution

In a Fisher-Porter glass reactor under Argon were introduced 45 mg of Ni(COD)₂ (0.164 mmol), 50 mL of toluene and 48 mg of *n*-octylsilane (0.33 mmol, 2 eq.), giving a pale yellow solution. The mixture was heated at 55 °C during 30 min, then the reactor was evacuated and pressurized with 4 bar of H₂ during 12 h. A brown colloidal solution containing 3.3 μmol Ni/mL was obtained. It was cooled down and stored under argon. Nanoparticles of < 2 nm diameter were obtained, as estimated by transmission electron microscopy.

S.2.2 NiO colloidal solution

51.8 mL of Ni₃Si₂ colloidal solution (0.17 mmol Ni, 10 mg Ni) were exposed to dry air, under agitation, during 30 min.

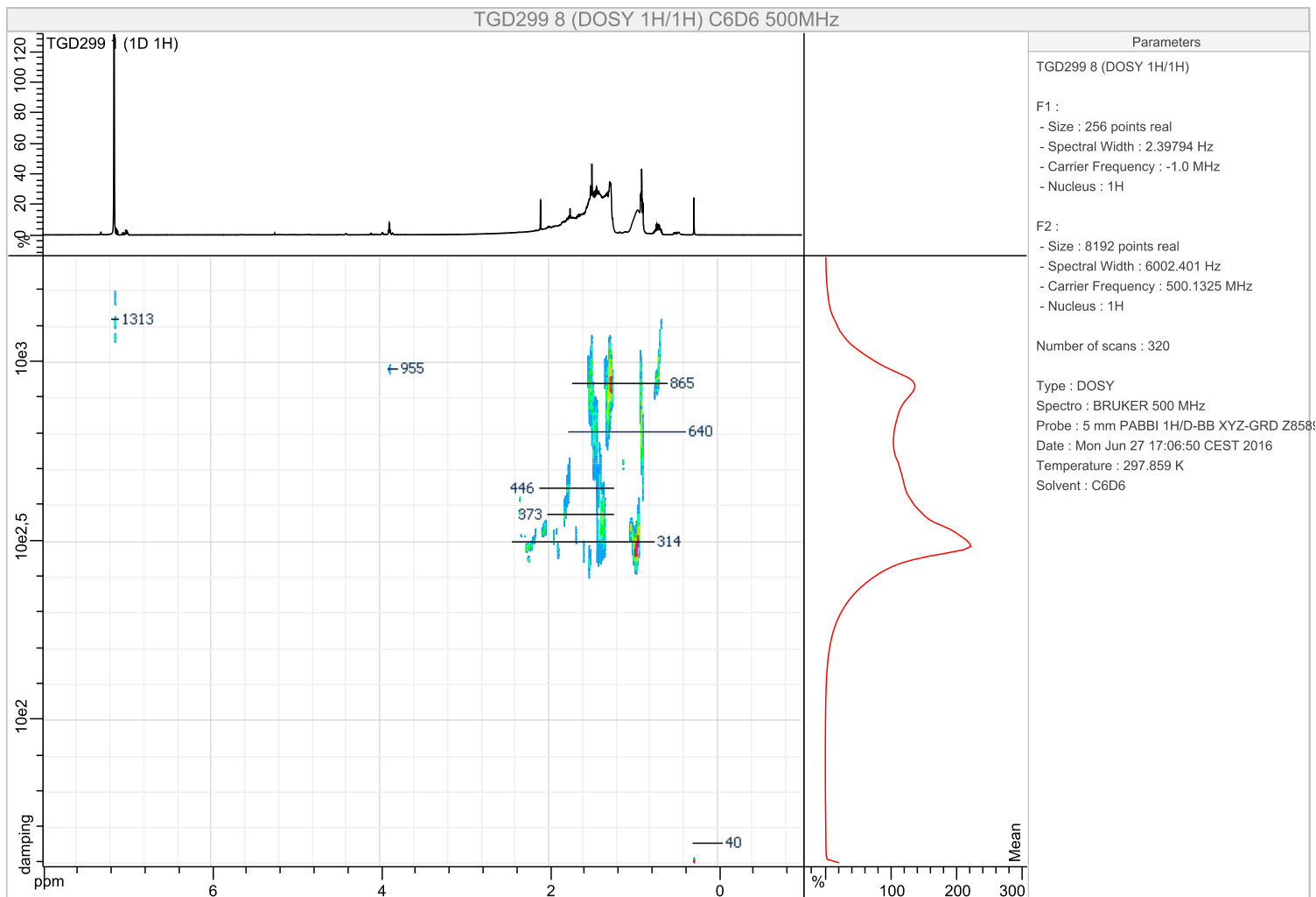
S.2.3 Ni/SiO₂

51.8 mL of NiO colloidal solution were concentrated under reduced pressure to a volume of 4 mL. The solution was then added drop-by-drop to 2 g of compacted fumed silica, under mechanical agitation. The solid was then calcinated with a flow of dry air of 40 mL min⁻¹ with a temperature ramp of 1 °C min⁻¹ to 500 °C and maintained at 500 °C during 1 h. The solid was then reduced with a hydrogen flow of 40 mL min⁻¹ with a temperature ramp of 1 °C min⁻¹ to 500 °C and maintained at 500 °C during 1 h. A grey solid containing 0.5% Ni w/w was obtained.

S.3 Ni₃Si₂ colloidal solution DOSY

The diffusion-ordered spectroscopy spectrum was acquired at the Centre Commun de RMN of Université Lyon 1 at 298 K on a AV 500 MHz Avance III Bruker spectrometer.

The Ni₃Si₂ colloidal solution was evaporated to dryness, then redissolved in C₆D₆ and transferred in a NMR tube equipped with a J. Young valve under argon.



Using the Stokes-Einstein law

$$D = \frac{k_B T}{6\pi\eta r}$$

the hydrodynamic radius can be estimated as

$$r = \frac{k_B T}{6\pi\eta D}$$

with $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$, $T = 298 \text{ K}$ and $\eta = 0.636 \text{ cP}$ (viscosity of C_6D_6 at 298 K)¹.

The signal attributed to the Ni_3Si_2 colloid having a diffusion coefficient of $314 \mu\text{m}^2 \text{ s}^{-1}$, hydrodynamic radius of 1.1 nm, and thus a hydrodynamic diameter of 2.2 nm was estimated, with 1 nm attributed to presence of the ligands.

S.4 Catalytic tests

In a Schlenk tube equipped with a magnetic stirrer and under argon were introduced 0.92 mL of triethoxysilane ((EtO)₃SiH, 5 mmol, 0.82 g), 1.06 mL of triethoxyvinylsilane ((EtO)₃SiCHCH₂, 0.96 g, 5 mmol, 1 eq.), 0.5 mL of dodecane (internal standard) and 3 mL of Ni colloidal solution (0.01 mmol Ni, 0.002 eq.) or 145 mg of silica-supported catalyst (0.01 mmol Ni, 0.002 eq.) and 3 mL of toluene. The mixture is heated at 120 °C under agitation. Samples are taken at regular interval, filtered with a 0.45 µm syringe filter, exposed to air and analyzed by gas chromatography.

S.5 Gas chromatography

Gas chromatography was performed on an Agilent 6890 Network Gas Chromatograph equipped with a Macherey-Nagel Optima® 5 column (10 m × 0.1 mm × 0.1 µm, 5% phenyl - 95% polydimethylsiloxane) and a flame ionization detector (FID). The injected volume was 1 µL, with a split ratio of 1:5000, in an injection chamber at 250 °C and 0.5 bar. The vector gas was H₂ at 0.4 mL min⁻¹ at 1.5 bar, corresponding to 50 cm s⁻¹. The oven temperature was 50 °C during 30 s, then a ramp at 50 °C min⁻¹ until 250 °C, then 250 °C during 30 s.

In these conditions, the retention times were as following:

Table 1 Retention times

Molecule	Retention time (min)
Toluene	0.89
Et ₃ SiH	0.96
(EtO) ₃ SiVi	1.72
(EtO) ₃ SiH	1.76
TEOS	1.83
Dodecane	2.32
[(EtO) ₃ SiCH] ₂	3.41
[(EtO) ₃ SiCH ₂] ₂	3.44
Dimers	3.7-3.9

Calibration curves of the analytes were done by injecting mixtures with different analyte/dodecane ratios and plotting the molar quantities ratio ($\frac{A_{analyte}}{A_{dodecane}}$) versus the areas ratio ($\frac{n_{analyte}}{n_{dodecane}}$).

The following molar response coefficients versus dodecane were obtained:

S.6 Si balance

A silicon balance was calculated for both catalytic tests by dividing the sum of all Si atoms in the reaction mixture by the sum of all Si atoms in the starting mixture:

$$Si\ balance = \frac{\sum n_{Si(products)}}{\sum n_{Si(starting\ mixture)}}$$

Table 2 Response coefficients versus dodecane

Molecule	Response coefficient versus dodecane
Et_3SiH	0.35
$(\text{EtO})_3\text{SiVi}$	0.54
$(\text{EtO})_3\text{SiEt}$	0.54
$[(\text{EtO})_3\text{SiCH}]_2$	1.06
$[(\text{EtO})_3\text{SiCH}_2]_2$	1.06

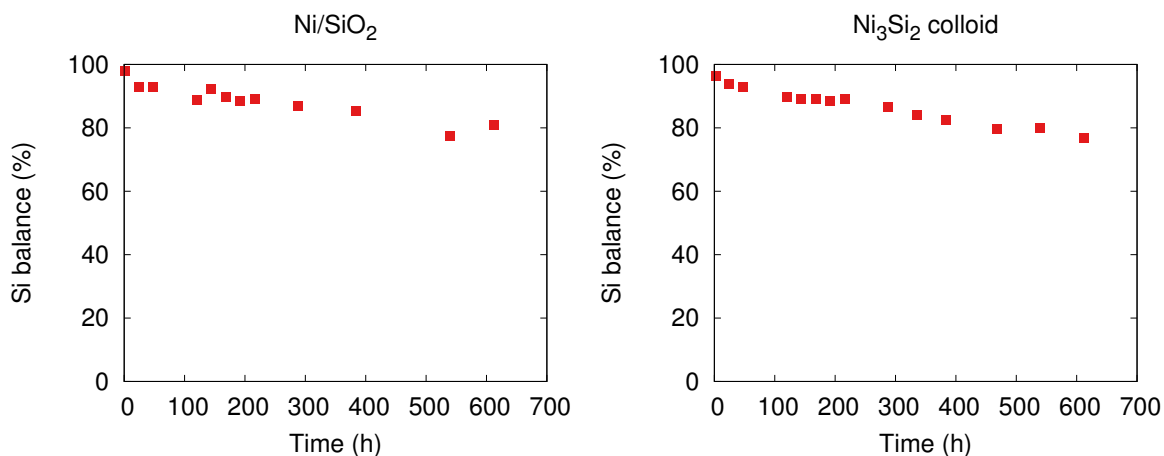


Fig. S1 Evolution of the Si balance with time.

For both catalytic tests, the Si balance decreased over time but was higher than 90% during 300 h and reached 90% after 650 h (Figure S 1). The non-detected products may be a combination of lighter products of silane redistribution and oligomers by dehydrogenative condensation.

References

- 1 M. Holz, X. Mao, D. Seiferling and A. Sacco, *J. Chem. Phys.*, 1996, **104**, 669–679.