Supporting Information

Molecular Control of the Catalytic Properties of Rhodium Nanoparticles in Supported Ionic Liquid Phase (SILP) Systems

Alexis Bordet,[†] *Gilles Moos,*[†,§] *Calum Welsh,*[‡] *Peter Licence,*[‡] *Kylie L. Luska,*[§] *Walter Leitner*[†,§*]

†Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany.

‡The University of Nottingham, School of Chemistry, Clifton Blvd, Nottingham NG7 2RD, United Kingdom.

§Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany.

* E-mail: walter.leitner@cec.mpg.de. Tel: (+49) 241-80-26481; Fax: (+49) 241-80-22177.

Safety Warning

High-pressure experiments with compressed $H_{2(g)}$ must be carried out only with appropriate equipment and under rigorous safety precautions.

General

All syntheses of non-commercial compounds were performed under argon either by using Schlenk techniques or in a glove box. Furfuralacetone was synthesized according to known literature methods and was purified by sublimation prior to use. Catalyst solutions and substrates were prepared under air. [Rh(allyl)$_3$] was synthesized according to known literature methods. All other chemicals and solvents were purchased from commercial sources and used without purification.

Experimental section

1. Analytics

^{1}H and ^{13}C NMR spectra were calibrated to TMS using the residual solvent signal. High-pressure experiments were performed using in-house engineered 10 and 20 mL stainless steel finger autoclaves. Catalytic reactions were performed in glass inlets using a magnetic stir bar (500 rpm) and an aluminum heating block. Gas chromatography (GC) was performed on a Thermo Scientific Chromatograph Trace GC Ultra equipped with a CP-Wax52 CB column from Agilent. Brunauer-Emmett-Teller (BET) measurements were performed on a Quadrasord SI automated Surface Area and Pore Size Analyzer from Quantachrome Instruments and the data analysis using QuadraWin 5-04. Inductively coupled plasma (ICP) was performed at Mikroanalytisches Laboratorium Kolbe on a Perkin Elmer Analyst 200 Atomic Absorption Spectrometer. Transmission electron microscopic (TEM) images were collected using a 200 kV electron microscope with cold field emitter and CCD-camera (Hitachi HF-2000).

XP spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al Kα source (hν = 1486.6 eV), hybrid (magnetic/electrostatic) optics, concentric

hemispherical analyser, a multi-channel plate and delay line detector (DLD) with an X-ray incident angle of 30° and a collection angle of 0° (both relative to the surface normal). X-ray source was operated at 10 mA emission current and 12 kV anode potential. All spectra were recorded using an entrance aperture of 300 × 700 µm with pass energy of 80 eV for survey scans and 20 eV for high resolution scans. Charge neutralisation (used for solid samples only) was applied using a standard Kratos charge neutraliser consisting of a filament, coaxial with the electrostatic and magnetic transfer lenses, and a balance plate which creates a potential gradient between the neutraliser and sample. Charge neutralisation was applied at 1.9 A filament current and 3.3 V balance plate voltage. Sample stubs were earthed via the instrument stage using a standard BNC connector. Room temperature ionic liquid samples were prepared by placing a small drop (≈10 mg) of ionic liquid onto a stainless steel multi-sample bar; solid samples were fixed to the bar using double-sided adhesive tape. All samples were pre-pumped in a preparative chamber to pressures lower than 1×10^{-6} mbar before transfer into the main analytical chamber. It is important to note that Rh scans should be measured first such that the native state of the metal is recorded before extended exposure to the X-ray illumination. In designing scan parameters, Rh should be measured early in sequences and the illumination area should be varied to ensure sample homogeneity and also to minimise the impact of the photochemistry to give rise to irradiative changes in oxidation state etc.
All XPS data were analysed using the CASAXPS software.

2. Synthesis of Ionic liquids, Supported Ionic Liquid Phases and Rhodium Catalysts

2.1 Synthesis of Ionic Liquids

2.1.1 1-Octyl-3-(3-triethoxysilylpropyl)imidazolium Bromide

1-(3-triethoxysilylpropyl)imidazole (10.1 g, 37.1 mmol) and octyl bromide (8.9 g, 46.3 mmol) were dissolved in toluene (50 mL) and stirred under reflux at 130°C for 18 h. The resulting mixture was washed 3 times with pentane (3x40 mL). The product was dried *in vacuo* to yield a viscous, yellowish liquid (4.86 g, 90%).
^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ (ppm) = 10.14 (s, 1H, NCHN), 7.90 (m, 2H, NCHCHN), 4.45 (m, 4H, NCH_2), 3.82 (q, *J* = 7.0 Hz, 6H, OCH_2), 2.01-1.68 (m, 4H, CH_2), 1.36 (m, 10H, CH_2), 1.19 (t, *J* = 7.0 Hz, 9H, OCH_2CH_3), 0.87 (t, *J* = 7.3 Hz, 3H, CH_3), 0.63 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ (ppm) = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_2), 32.0 (s, 1C, CH_2), 24.3 (s, 1C, CH_2), 19.4 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 13.2 (s, 1C, CH_3), 7.0 (s, 1C, $SiCH_2$).
HRMS/ESI(+/-) (CH_2Cl_2): m/z = 385.288096 and 78.918900, calcd. for $[C_{20}H_{41}N_2O_3Si]^+$ = 385.288180 and $[Br]^-$ = 78.918890.

2.1.2 1-Octyl-3-(3-triethoxysilylpropyl)imidazolium trifluoromethylsulfonate

1-3-triethoxysilylpropyl imidazole (4.10 g, 15.0 mmol) and octyltriflate (3.93 g, 15.0 mmol) were dissolved respectively in 15 and 10 mL DCM. The solution containing the imidazole derivative was cooled down to 0°C, and the octyltriflate solution was added dropwise over 5 min. The mixture was stirred at 0°C for 1 h, and then allowed to warm up to room temperature. Mixture stirred overnight. After reaction, the solvent was evaporated under vacuum, yielding a pale yellow/brown oil (7.38 g, 92%).

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) = 9.10 (s, 1H, NCHN), 7.74 (m, 2H, NCHCHN), 4.29 (m, 4H, NCH_2), 3.72 (q, J = 7.0 Hz, 6H, OCH_2), 2.06-1.82 (m, 4H, CH_2), 1.26 (m, 10H, CH_2), 1.08 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.77 (t, J = 7.3 Hz, 3H, CH_3), 0.52 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ (ppm) = 137.0 (s, 1C, NCHN), 126.7 (s, 1C, NCHCHN), 123.6 (s, 1C, NCHCHN), 119.9 (q, J_{CF} = 327 Hz, 1C, CF_3), 59.0 (s, 3C, OCH_2), 52.7 (s, 1C, NCH_2), 50.6 (s, 1C, NCH_2), 32.5 (s, 1C, CH_2), 30.8 (s, 1C, CH_2), 30.1 (s, 1C, CH_2), 29.3 (s, 1C, CH_2), 26.8 (s, 1C, CH_2), 25.6 (s, 1C, CH_2), 25.0 (s, 1C, CH_2), 23.3 (s, 1C, CH_2), 18.7 (s, 3C, OCH_2CH_3), 14.3 (s, 1C, CH_3), 7.8 (s, 1C, $SiCH_2$).
HRMS/ESI(+/-) (CH_2Cl_2): m/z = 385.288096 and 148.952578, calcd for $[C_{20}H_{41}N_2O_3Si]^+$ = 385.288160 and $[CF_3O_3S]^-$ = 148.952500.

2.1.3 1-Octyl-3-(3-triethoxysilylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide

1-octyl-3-(3-triethoxysilylpropyl)imidazolium bromide (5.6 g, 12.0 mmol) and bis(trifluoromethane)sulfonimide lithium salt (3.6 g, 12.6 mmol) were dissolved in water (20 mL) and stirred at rt for 1 h. DCM (50 mL) was added and the organic phase was washed with water (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous, yellow/brown liquid (6.72 g, 84%).

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) = 9.14 (s, 1H, NCHN), 7.83 (m, 2H, NCHCHN), 4.38 (m, 4H, NCH_2), 3.82 (q, J = 7.0 Hz, 6H, OCH_2), 2.11-1.94 (m, 4H, CH_2), 1.36 (m, 10H, CH_2), 1.18 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.87 (t, J = 7.3 Hz, 3H, CH_3), 0.62 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ (ppm) = 136.8 (s, 1C, NCHN), 123.7 (s, 1C, NCHCHN), 123.6 (s, 1C, NCHCHN), 119.2 (q, J_{CF} = 327 Hz, 2C, CF_3), 59.0 (s, 3C, OCH_2), 52.8 (s, 1C, NCH_2), 50.7 (s, 1C, NCH_2), 32.5 (s, 1C, CH_2), 30.7 (s, 1C, CH_2), 29.8 (s, 1C, CH_2), 29.1 (s, 1C, CH_2), 27.3 (s, 1C, CH_2), 26.9 (s, 1C, CH_2), 25.0 (s, 1C, CH_2), 23.3 (s, 1C, CH_2), 18.7 (s, 3C, OCH_2CH_3), 14.3 (s, 1C, CH_3), 7.8 (s, 1C, $SiCH_2$).
HRMS/ESI(+) (CH_2Cl_2): m/z = 385.288096 and 279.917850, calcd for $[C_{20}H_{41}N_2O_3Si]^+$ = 385.288160 and $[C_2F_6N_1O_4S_2]^-$ = 279.917920.

2.1.4 1-Octyl-3-(3-triethoxysilylmethyl)imidazolium Iodide

Triethoxysilylmethyl Iodide (9.31 g, 30.6 mmol) was dissolved in 25 mL toluene (dry, degased) and added to a solution of Octylimidazole (6.07 g, 33.7 mmol, dried 2 h under vacuum prior to use) in toluene (20 mL). The resulting mixture was stirred under reflux at 130°C for 18 h. The resulting mixture was washed 3 times with pentane (3x20 mL). The product was dried *in vacuo* to yield a viscous, yellowish liquid (13.91 g, 94%).

^{1}H NMR (300 MHz, H_2O): δ (ppm) = 8.66 (s, 1H, NCHN), 7.48 (m, 2H, NCHCHN), 4.20 (m, 2H, NCH_2), 3.90 (m, 4H,) 3.63 (q, J = 7.0 Hz, 6H, OCH_2), 1.88-1.83 (m, 2H, CH_2), 1.28 (m, 10H, CH_2), 1.19 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.84 (t, J = 7.3 Hz, 3H, CH_3).
^{13}C NMR (150 MHz, H_2O): δ (ppm) = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_2), 32.0 (s, 1C, CH_2), 31.4 (s, 1C, CH_2), 30.7 (s, 1C, CH_2), 29.6 (s, 1C, CH_2), 27.1 (s, 1C, CH_2), 24.3 (s, 1C, CH_2), 19.4 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 13.2 (s, 1C, CH_3), 7.0 (s, 1C, $SiCH_2$).
HRMS/ESI(+)(CH_2Cl_2): m/z = 357.256796 and 126.905022, calcd for $[C_{18}H_{37}N_2O_3Si]^+$ = 357.256990 and $[I]^-$ = 126.905030.

2.1.5 1-Octyl-3-(3-triethoxysilylmethyl)imidazolium bis(trifluoromethylsulfonyl)imide

1-Octyl-3-(3-triethoxysilylmethyl)imidazoliumbromide (5.8 g, 12.0 mmol) was dissolved in 5 mL dionized H_2O and $LiNTf_2$ (3.6 g, 12.6 mmol) was added as a powder (+ 5 mL H_2O to wash the vial). The mixture was stirred vigorously (1100 rpm) at room temperature for 1 h. After 1 h, addition of 50 mL DCM, and mixture stirred for 5 min. Organic phase washed 3 times with H_2O (3x 50 mL), dried over MgSO4, and solvent evaporated under vacuum. The product was dried *in vacuo* to yield a viscous, yellowish liquid (6.5 g, 85%).

^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ (ppm) = 9.00 (s, 1H, NCHN), 7.81 (d, 2H, NCHCHN), 4.40 (m, 2H, NCH_2), 4.07 (m, 2H,) 3.93 (q, *J* = 7.0 Hz, 6H, OCH_2), 1.96 (m, 2H, CH_2), 1.35 (m, 10H, CH_2), 1.27 (t, *J* = 7.0 Hz, 9H, OCH_2CH_3), 0.86 (t, *J* = 7.3 Hz, 3H, CH_3).
^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ (ppm) = 137.7 (s, 1C, NCHN), 125.1 (s, 1C, NCHCHN), 123.5 (s, 1C, NCHCHN), 119.3 (q, J_{CF} = 327 Hz, 2C, CF_3), 60.1 (s, 3C, OCH_2), 50.6 (s, 1C, NCH_2), 36.6 (s, 1C, CH_2), 32.4 (s, 1C, CH_2), 30.9 (s, 1C, CH_2), 29.8 (s, 1C, CH_2), 26.8 (s, 1C, CH_2), 23.3 (s, 1C, CH_2), 18.5 (s, 3C, OCH_2CH_3), 14.3 (s, 1C, CH_3).
HRMS/ESI(+/-) (CH_2Cl_2): m/z = 357.256796 and 279.917850, calcd for $[C_{18}H_{37}N_2O_3Si]^+$ = 357.256990 and $[C_2F_6N_1O_4S_2]^-$ = 279.917920.

2.1.6 1-Methyl-3-(3-triethoxysilylpropyl)imidazolium Iodide

Methylimidazole (1.9 g, 23 mmol, dried 2h under vacuum prior to use) was dissolved in 20 mL dry and degased toluene. Triethoxysilylpropyl Iodide (11.6 g, 7.9 mL 35.0 mmol (65% Iodide, 35% chloride)) was dissolved in 25 mL toluene and added to the methyimidazole solution. The resulting mixture was stirred under reflux at 130°C for 18 h. The resulting mixture was washed 3 times with pentane (3x20 mL). The product was dried *in vacuo* to yield a viscous, brownish liquid (7.63 g, 80%).

^{1}H NMR (300 MHz, H_2O): δ (ppm) = 8.75 (s, 1H, NCHN), 7.50 (m, 2H, NCHCHN), 4.24 (m, 2H, NCH_2), 3.90 (s, 3H, NCH_3) 3.68 (q, *J* = 7.0 Hz, 6H, OCH_2), 2.03-1.93 (m, 2H, CH_2), 1.20 (t, *J* = 7.0 Hz, 9H, OCH_2CH_3), 0.66 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, H_2O): δ (ppm) = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_3), 24.3 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 7.0 (s, 1C, $SiCH_2$).
HRMS/ESI(+) (CH_2Cl_2): m/z = 287.178342 and 126.905022, calcd for $[C_{13}H_{27}N_2O_3Si]^+$ = 287.178361 and $[I]^-$ = 126.905030.

2.1.7 1-Methyl-3-(3-triethoxysilylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide

1-methyl-3-(3-triethoxysilylpropyl)imidazoliumiodide (4.97 g, 12.0 mmol) and bis(trifluoromethane)sulfonimide lithium salt (3.6 g, 12.6 mmol) were dissolved in water (5 mL) + DCM (5 mL) and stirred at rt for 1 h. Ethyl acetate (40 mL) was added and the organic phase was washed with water (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous, yellow/brown liquid (3.2 g, 47%).

^{1}H NMR (300 MHz, H_2O): δ (ppm) = 8.94 (s, 1H, NCHN), 7.73 (m, 2H, NCHCHN), 4.34 (m, 1H, NCH_2), 4.04 (q, *J* = 7.0 Hz, 6H, OCH_2) 3.81 (s, 3H, NCH_3), 1.96 (m, 3H, NCH_3), 1.19 (t, *J* = 7.0 Hz, 9H, OCH_2CH_3), 0.70 (m, 2H, $SiCH_2$).

^{13}C NMR (150 MHz, H_2O): δ (ppm) = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 119.0 (q, J_{CF} = 327 Hz, 2C, CF_3), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_3), 24.3 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 7.0 (s, 1C, $SiCH_2$).
HRMS/ESI(+) (CH_2Cl_2): m/z = 287.178342 and 279.917850, calcd for $[C_{13}H_{27}N_2O_3Si]^+$ = 287.178361 and $[C_2F_6N_1O_4S_2]^-$ = 279.917920.

2.1.8 1-Decyl-3-(3-triethoxysilylpropyl)imidazolium bromide

1-(3-triethoxysilylpropyl)imidazole (10.1 g, 37.1 mmol) and decyl bromide (10.2 g, 46.3 mmol) were dissolved in toluene (50 mL) and stirred under reflux at 130°C for 18 h. The resulting mixture was washed 3 times with pentane (3x40 mL). The product was dried *in vacuo* to yield a viscous, yellowish liquid (15.6 g, 85%).

^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ (ppm) = 10.23 (s, 1H, NCHN), 7.92 (m, 2H, NCHCHN), 4.46 (m, 4H, NCH_2), 3.82 (q, J = 7.0 Hz, 6H, OCH_2), 2.01-1.68 (m, 4H, CH_2), 1.38-1.22 (m, 14H, CH_2), 1.19 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.89 (t, J = 7.3 Hz, 3H, CH_3), 0.63 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ (ppm) = 137.9 (s, 1C, NCHN), 123.4 (s, 1C, NCHCHN), 123.2 (s, 1C, NCHCHN), 59.0 (s, 3C, OCH_2), 52.4 (s, 1C, NCH_2), 50.3 (s, 1C, NCH_2), 32.6 (s, 1C, CH_2), 30.3 (s, 1C, CH_2), 30.2(s, 1C, CH_2), 30.1 (s, 1C, CH_2), 29.8 (s, 1C, CH_2), 26.9 (s, 1C, CH_2), 25.1 (s, 1C, CH_2), 23.3 (s, 1C, CH_2), 19.4 (s, 1C, CH_2), 18.7 (s, 3C, OCH_2CH_3), 14.4 (s, 1C, CH_3), 7.8 (s, 1C, $SiCH_2$)
HRMS/ESI(+) (CH_2Cl_2): m/z = 413.319784 and 78.918900, calcd. for $[C_{22}H_{45}N_2O_3Si]^+$ = 413.319779 and $[Br]^-$ = 78.918890.

2.1.9 1-Decyl-3-(3-triethoxysilylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide

1-decyl-3-(3-triethoxysilylpropyl)imidazolium bromide (10.0 g, 20.3 mmol) and bis(trifluoromethane)sulfonimide lithium salt (6.1 g, 21.3 mmol) were dissolved in water (15 mL) and stirred at rt for 1 h. DCM (50 mL) was added and the organic phase was washed with water (3x50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous, yellow/brown liquid (13.4 g, 95%).

^{1}H NMR (300 MHz, H_2O): δ (ppm) = 9.14 (s, 1H, NCHN), 7.83 (s, 2H, NCHCHN), 4.41-4.36 (m, 4H, NCH_2), 3.84-378 (q, J = 7.0 Hz, 6H, OCH_2), 2.01-1.68 (m, 2H, CH_2), 1.36-1.27 (m, 14H, CH_2), 1.19 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.89 (t, J = 7.3 Hz, 3H, CH_3), 0.63 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, H_2O): δ (ppm) = 136.8 (s, 1C, NCHN), 123.7 (s, 1C, NCHCHN), 123.6 (s, 1C, NCHCHN), 59.0 (s, 3C, OCH_2), 52.8 (s, 1C, NCH_2), 50.6 (s, 1C, NCH_2), 32.6 (s, 1C, CH_2), 30.7 (s, 1C, CH_2), 30.5 (s, 1C, CH_2), 30.3 (s, 1C, CH_2), 30.2(s, 1C, CH_2), 30.1 (s, 1C, CH_2), 29.9 (s, 1C, CH_2), 29.7 (s, 1C, CH_2) 26.8 (s, 1C, CH_2), 24.9 (s, 1C, CH_2), 23.3 (s, 1C, CH_2), 18.7 (s, 3C, OCH_2CH_3), 14.4 (s, 1C, CH_3), 7.8 (s, 1C, $SiCH_2$).
HRMS/ESI(+) (CH_2Cl_2): m/z = 413.319784 and 279.917850, calcd. for $[C_{22}H_{45}N_2O_3Si]^+$ = 413.319779 and $[C_2F_6N_1O_4S_2]^-$ = 279.917920.

2.1.10 1-butyl-3-(3-triethoxysilylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide

1-butyl-3-(3-triethoxysilylpropyl)imidazolium chloride (3.23 g, 8.85 mmol) and bis(trifluoromethane)sulfonimide lithium salt (2.65 g, 9.24 mmol) were dissolved in water (15 mL) and stirred at rt for 10 h. The aqueous phase was extracted with DCM (5x20 mL) and the combined organic phase was washed with water (3x20 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous, colourless liquid (4.86 g, 90%).

^{1}H NMR (300 MHz, H_2O): δ (ppm) = 8.78 (s, 1H, NCHN), 7.31 (m, 2H, NCHCHN), 4.18 (m, 4H, NCH_2), 3.78 (q, J = 7.0 Hz, 6H, OCH_2), 2.01-1.68 (m, 4H, CH_2), 1.34 (m, 2H, CH_2), 1.19 (t, J = 7.0 Hz, 9H, OCH_2CH_3), 0.93 (t, J = 7.3 Hz, 3H, CH_3), 0.55 (m, 2H, $SiCH_2$).
^{13}C NMR (150 MHz, H_2O): δ (ppm) = 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 119.9 (q, J_{CF} = 327 Hz, 2C, CF_3), 58.7 (s, 3C, OCH_2), 52.0 (s, 1C, NCH_2), 50.0 (s, 1C, NCH_2), 32.0 (s, 1C, CH_2), 24.3 (s, 1C, CH_2), 19.4 (s, 1C, CH_2), 18.1 (s, 3C, OCH_2CH_3), 13.2 (s, 1C, CH_3), 7.0 (s, 1C, $SiCH_2$).
HRMS/ESI(+) (MeOH): m/z = 329.229647 and 279.917850, calcd for $[C_{16}H_{33}N_2O_3Si]^+$ = 329.229691 and $[C_2F_6N_1O_4S_2]^-$ = 279.917920.

2.2 *General procedure for the synthesis of Supported Ionic Liquid Phases (SILPs)*

[1-octyl-3-(3-triethoxysilylpropyl)imidazolium]NTf_2 (5.49 g, 8.80 mmol) was dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO_2 (10.0 g in 50.0 mL toluene). The resulting mixture was refluxed for 18 h. Upon removal of the organic phase, the SILP was washed with DCM (3x25 mL) and dried *in vacuo*. The organic phases were combined and solvent removed to determine the residual quantity of IL not grafted onto the dehydroxylated SiO_2 (Total IL Loading = Theoretical Loading – Recovered Residual IL).

N.B. The Si-Oct support was synthesized following a similar procedure, using triethoxy(octyl)silane instead of an ionic liquid.

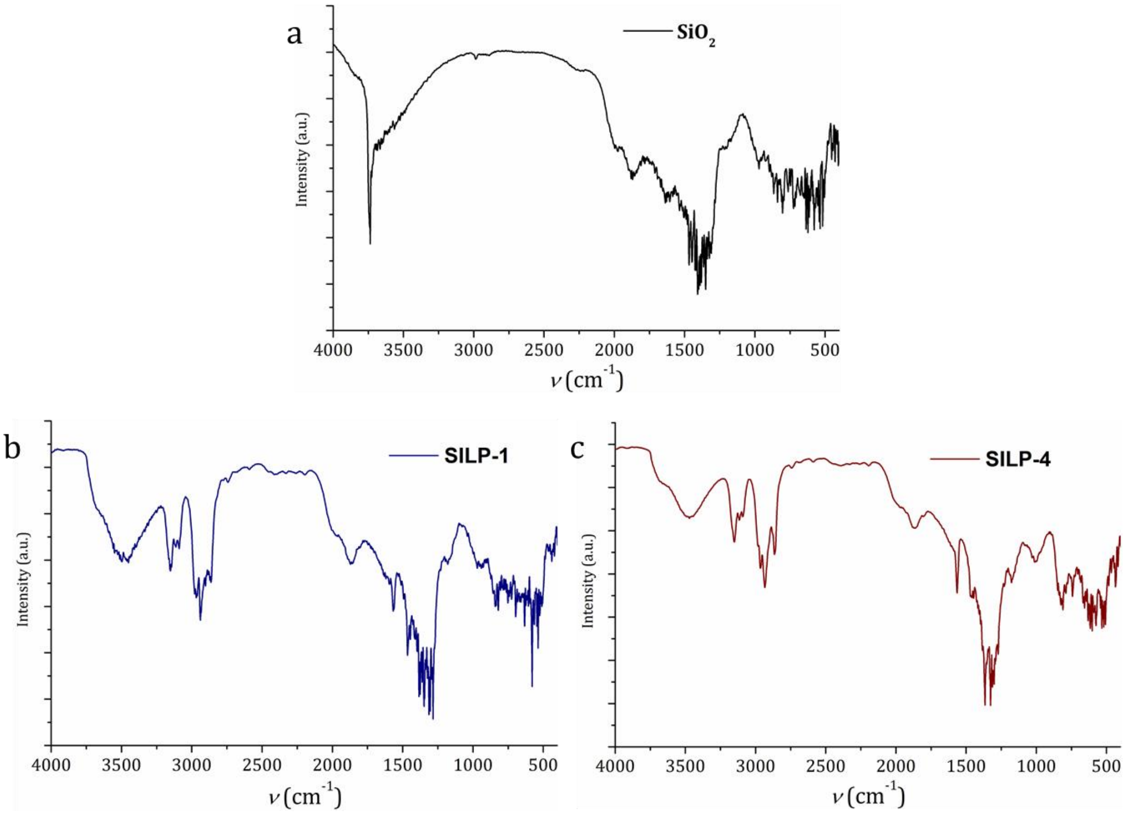

Figure S1. Examples of DRIFT IR analysis of a) dehydroxylated SiO_2, b) **SILP-1**, c) **SILP-4**.

2.3 General procedure for the synthesis of Rh@SILPs catalysts (theoretical loading: 0.1 $mmol_{Rh}.g^{-1}$)

The synthesis of Rh NPs immobilized on SILPs (Rh@SILPs) involved the wet impregnation of the SILP (0.50 g) with a solution of [Rh(allyl)$_3$] (11.3 mg, 0.05 mmol) in dichloromethane (DCM) (5 mL). Upon addition of the [Rh(allyl)$_3$] solution, the SILP transformed from a white to a bright yellow colour, which indicated the adsorption of the Rh precursor into the SILP. Upon evaporation of the solvent in vacuo, the impregnated SILP powder was subjected to an atmosphere of H_2(g) (50 bar) at 100°C for 18 h. Under these conditions, the bright yellow powder turned black in colour and signified the formation of Rh NPs.

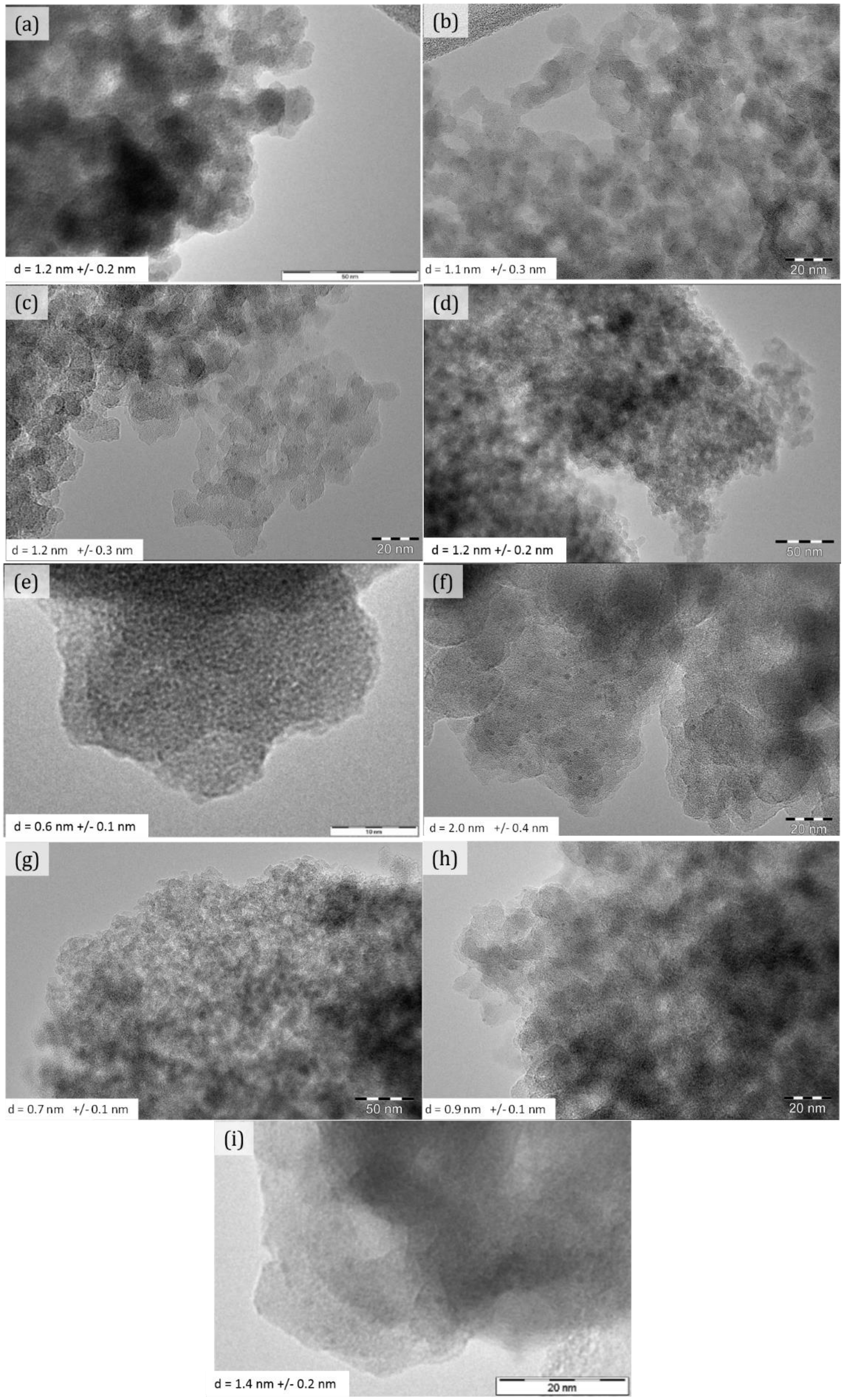

Figure S2. TEM characterization of Rh@: (a) SiO_2, (b) Si-Oct, (c) **SILP-1**, (d) **SILP-2**, (e) **SILP-3**, (f) **SILP-4**, (g) **SILP-5**, (h) **SILP-6**, (i) **SILP-7**.

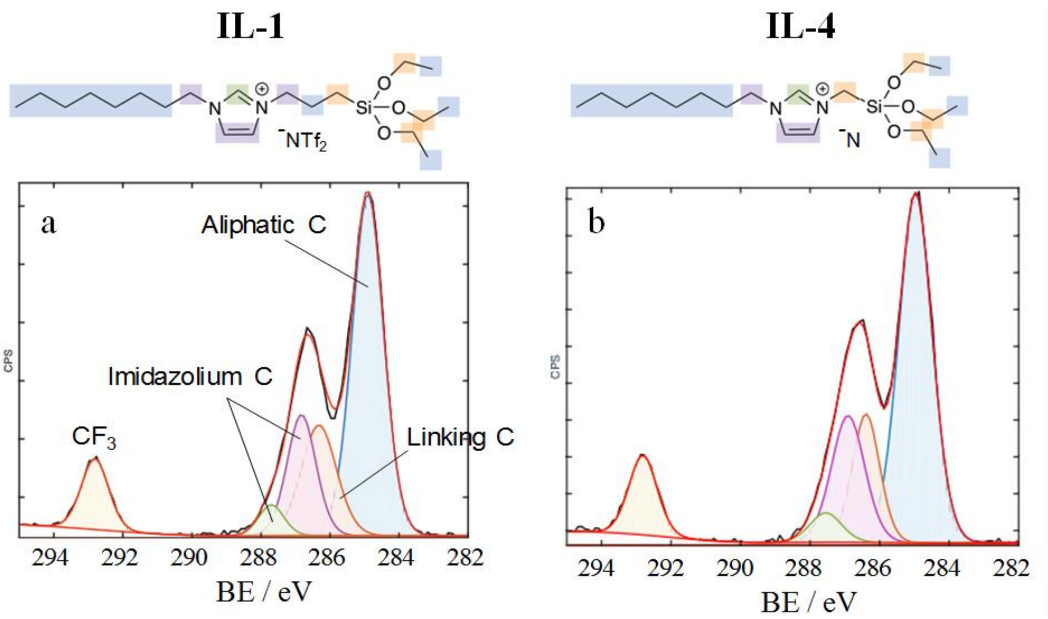

Figure S3. C 1s XP spectra of a) 1-Octyl-3-(3-triethoxysilylpropyl)imidazolium bis(trifluoromethylsulfonyl)imide (**IL-1**) and b) 1-Octyl-3-(3-triethoxysilylmethyl)imidazolium bis(trifluoromethylsulfonyl)imide (**IL-4**). XP spectra were charge corrected by referencing the aliphatic C 1s photoemission peak to 285.0 eV.

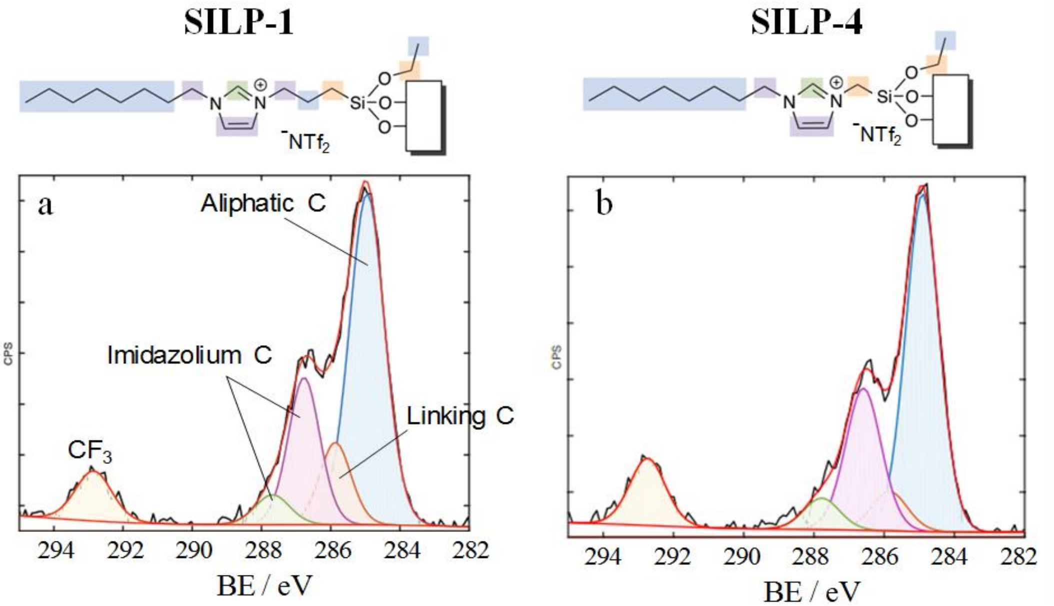

Figure S4. C 1s XP spectra of a) **SILP-1** and b) **SILP-2**.

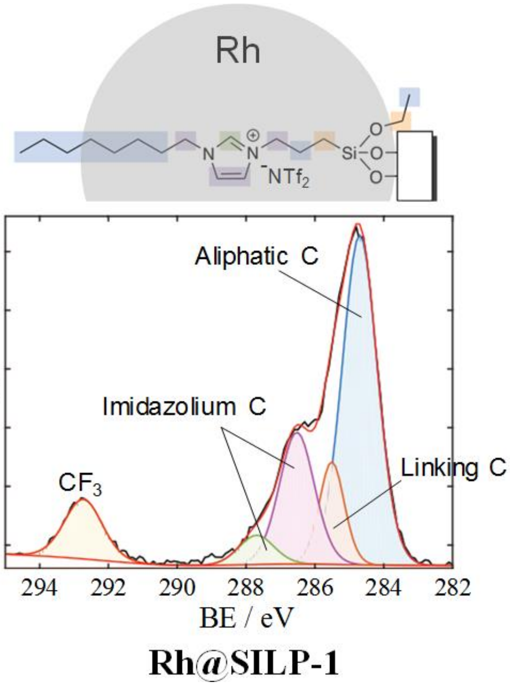

Figure S5. C 1s XP spectra of Rh@**SILP-1**.

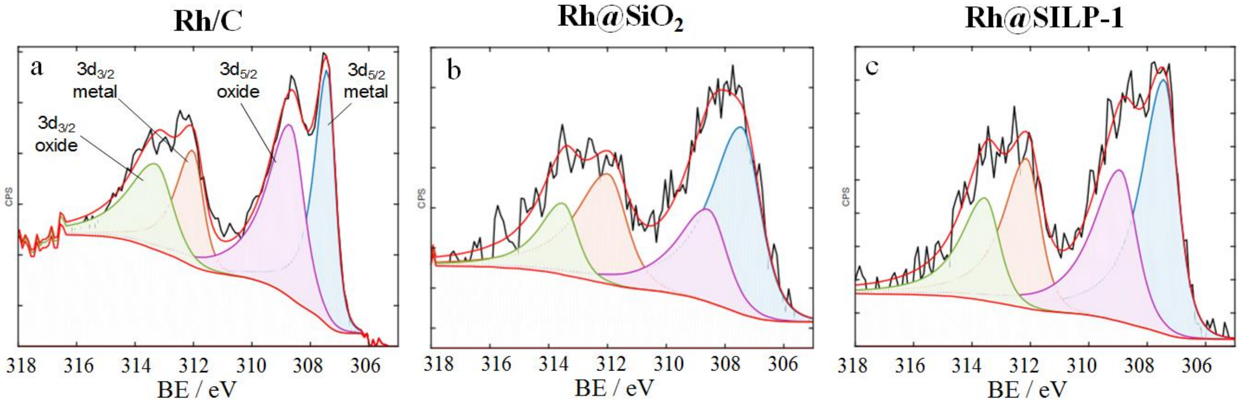

Figure S6. Rh 3d XP spectra of a) Rh/C, b) Rh@SiO$_2$ and c) Rh@**SILP-1**.

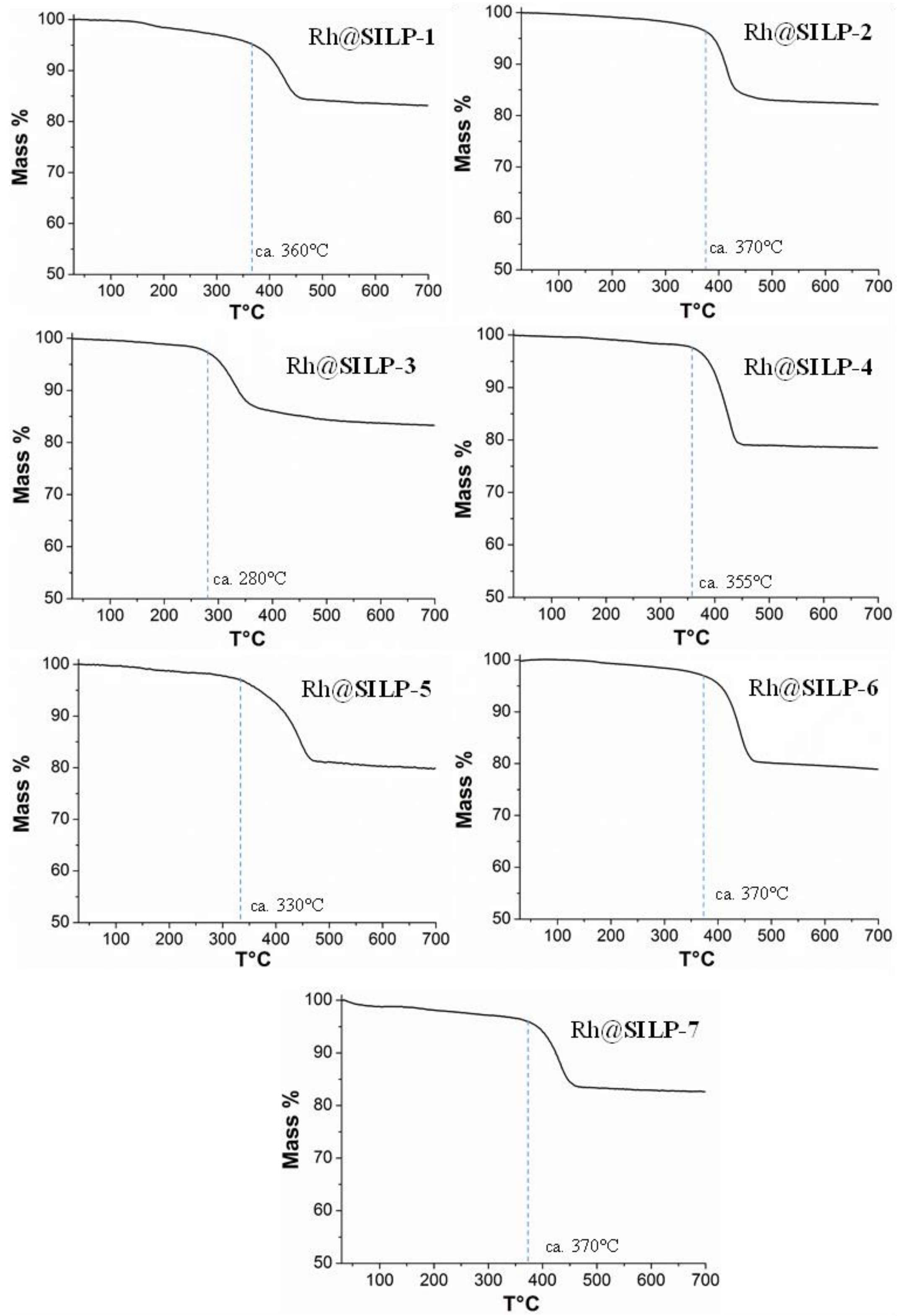

Figure S7. Thermal stability of the different Rh@SILP materials investigated by thermogravimetric analysis under Ar.

3. Catalysis

3.1 Catalysis in batch reactor

In a typical experiment, Rh@SILP (40 mg, 0.004 mmol Rh), furfuralacetone (0.4 mmol, 100 equiv.), and heptanes (0.5 mL) were combined in a glass insert and placed in a high-pressure autoclave. After purging the autoclave with H_2, the reaction mixture was stirred at 100°C in an aluminum heating block under 20 bar H_2. Once the reaction was finished, the reactor was cooled, carefully vented, and the reaction mixture was analyzed by GC using tetradecane as an internal standard.

3.2 Determination of TOFs

Turn over frequencies were determined using the following equation:

$$TOF = \frac{n(product_{/h})}{n(Rh) * \%(surface\ Rh)}$$

The %(surface Rh) were estimated for each catalyst by calculating the volume of the Ru NPs as well as the volume of the shell containing the first layer of Ru atoms (approximation: spherical NPs):

$$V_{NPs} = \frac{4}{3}\pi * r^3{}_{NPs}$$

$$V_{shell} = \frac{4}{3}\pi * (r^3{}_{NPs} - (\mathrm{r}_{NPs} - \mathrm{r}_{at\ Rh})^3)$$

with $r_{\mathrm{at\ Rh}} = 0.135$ nm

$$\%_{surface\ Rh} = \frac{V_{shell}}{V_{NPs}}$$

Table S1. Data used to estimate the % of surface Rh.

Catalyst	**NPs size** (nm)	**V_{NPs}** (nm^3)	**V_{shell}** (nm^3)	**Surface Rh** (%)
Rh@SiO$_2$	1.2 +/- 0.2	0.904	0.483	53.5
Rh@Si-Oct	1.1 +/- 0.3	0.697	0.397	57.0
Rh@**SILP-1**	1.2 +/- 0.3	0.904	0.483	53.5
Rh@**SILP-2**	1.2 +/- 0.2	0.697	0.397	57.0
Rh@**SILP-3**	0.6 +/- 0.1	0.113	0.094	83.4
Rh@**SILP-4**	2.0 +/- 0.4	4.187	1.477	35.3
Rh@**SILP-5**	0.7 +/- 0.1	0.180	0.138	76.8
Rh@**SILP-6**	0.9 +/- 0.1	0.382	0.251	65.7
Rh@**SILP-7**	1.4 +/- 0.2	1.436	0.681	47.4

In case of Table 3-5, TOFs for the production of **5** were estimated for 1 h reactions, for which the yield of **5** was low.

3.3 Catalysis in continuous flow reactor

A 70 mm CatCart was filled with Rh@SILP (250 mg, 0.025 mmol Rh) and placed into a flow reactor (H-Cube Pro). Prior to catalysis, the catalyst was heated at 100°C under a flow of heptane (0.5 mL.min^{-1}) and H_2 (20 bar; gas flow rate under standard conditions = 35 NmL.min^{-1}) for 30 min. The substrate solution (0.05 M furfuralacetone in heptane) was introduced into the system with a flow of H_2 (20 bar) and the reaction parameters (temperature=100°C, substrate flow=0.5 mL.min^{-1}, H_2 flow rate=35 NmL.min^{-1}) were set up. The system was allowed to equilibrate under the desired reaction conditions for 20 min before approximately 2 mL of reaction solution was collected. The reaction mixture was analyzed by GC using tetradecane as an internal standard.

Table S2: Catalysts properties before and after continuous flow catalysis (TEM, ICP and BET analysis).

	Before catalysis				**After catalysis**			
Catalyst	**NPs size** (nm)	**Rh content** (wt%)	**F content** (wt%)	**Surface area** (m^2.g^{-1})	**NPs size** (nm)	**Rh content** (wt%)	**F content** (wt%)	**Surface area** (m^2.g^{-1})
Rh@SiO_2	1.2	0.98	-	342.3	2.3	1.02	-	264.7
Rh@Si-Oct	1.1	0.83	-	305.1	2.1	0.76	-	279.8
Rh@**SILP-1**	1.2	0.81	3.77	222.4	1.4	0.90	3.68	222.7
Rh@**SILP-4**	2.0	0.95	4.97	187.2	2.3	1.06	5.05	188.1

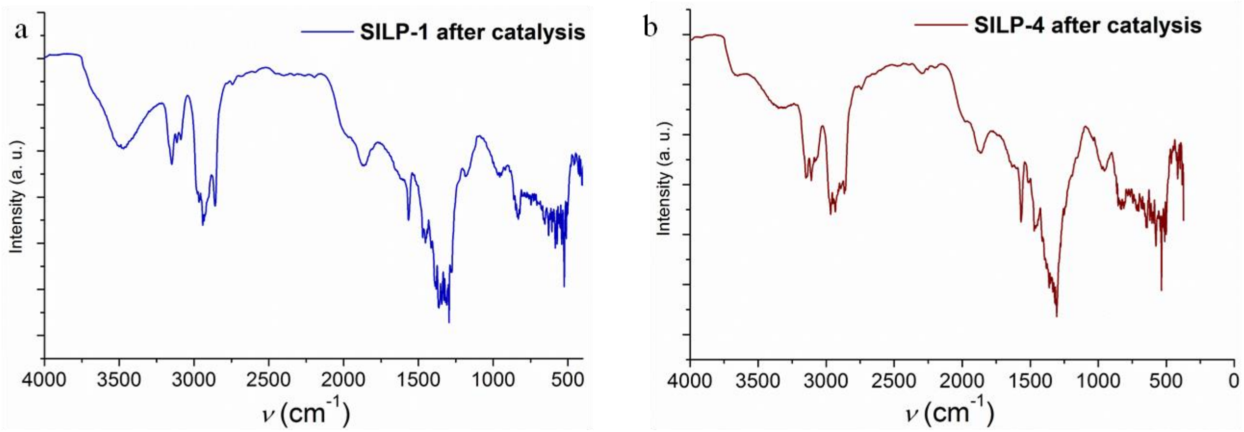

Figure S8. IR characterization of Rh@: (a) **SILP-1**, and (b) **SILP-4** after catalysis under continuous flow conditions.

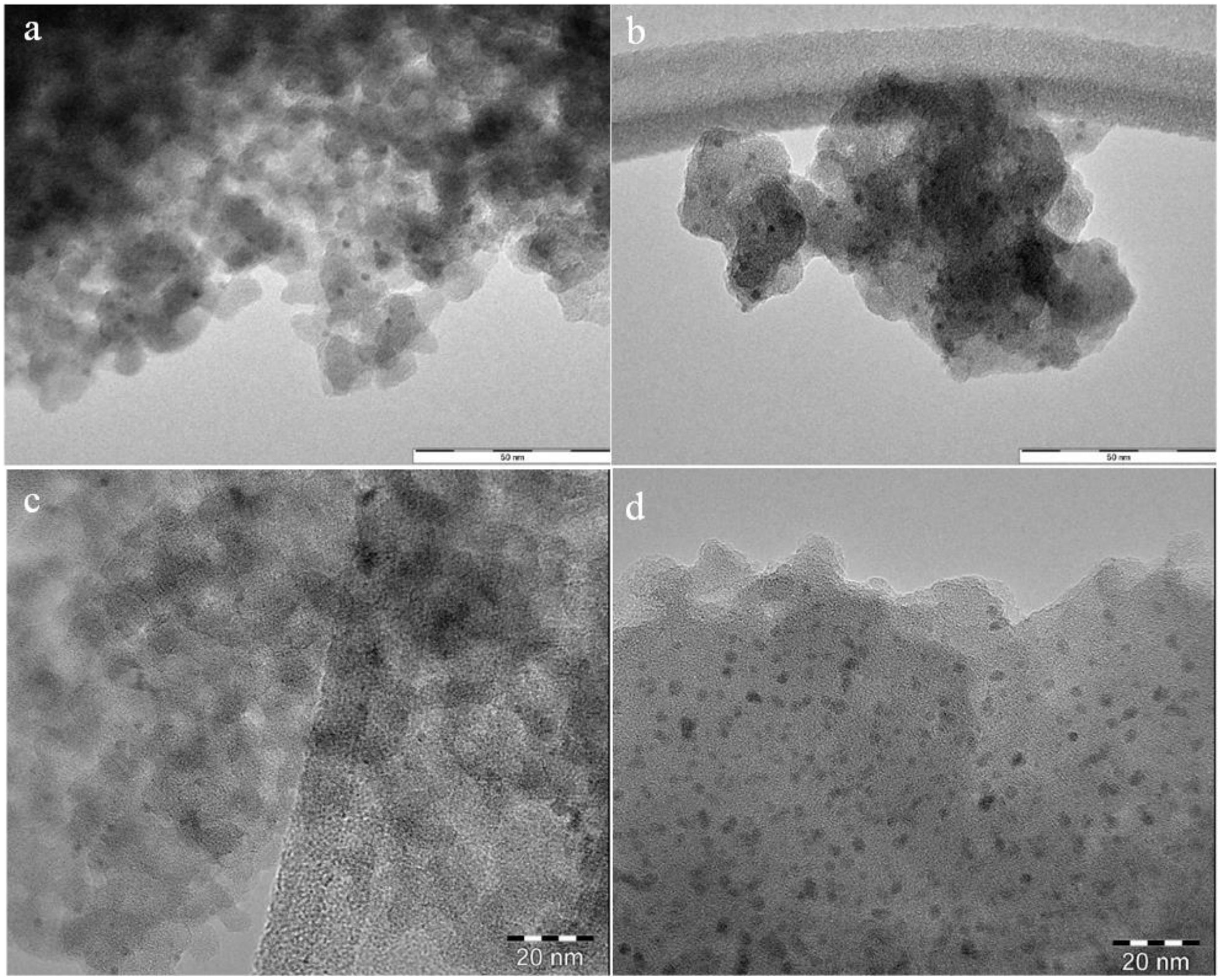

Figure S9. TEM characterization of Rh@: (a) SiO_2, (b) Si-Oct, (c) **SILP-1**, (d) **SILP-4** after catalysis under continuous flow conditions.

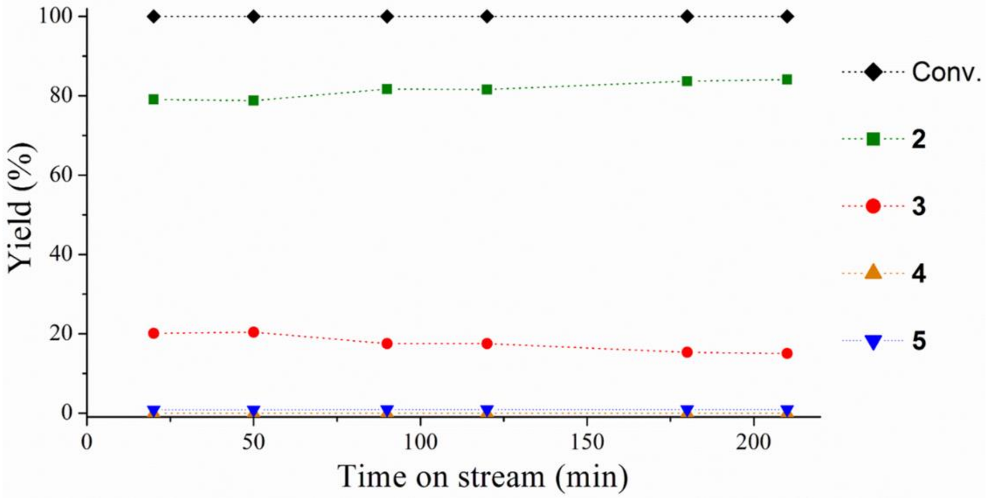

Figure S10. Hydrogenation of furfuralacetone (0.05 M in heptane, 1.0 mL.min^{-1}) using Rh@**SILP-4** (200 mg, 0.02 mmol Rh) under continuous flow conditions at 100°C and 20 bar H_2 (gas flow rate = 35 NmL.min^{-1}).