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Supplementary Information

Selective partial hydrogenation of alkynes to (Z)-alkenes with ionic liquid-doped nickel nanocatalysts at near ambient conditions

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Experimental

General methods

All manipulations involving the $[\text{Ni}(\text{COD})_2]$ complex were carried out in a *MBraun Labmaster 200* glovebox under an argon atmosphere.

Phenylacetylene was purchased from *Alfa Aesar*, diphenylacetylene was purchased from *Acros Organics*, dimethylacetylene dicarboxylate, 4-octyne, 1-octyne and 1-bromo-2-pentyne were purchased from *SigmaAldrich*, methyl non-2-ynoate and 1-ethynyl-4-methoxybenzene were purchased from *Maybridge*, trimethylsilyl-1-hexyne and 1-phenyl-2-trimethylsilylacetylene was purchased from *ABCR*. The organometallic precursor $[\text{Ni}(\text{COD})_2]$ was purchased from *ABCR*.

The ionic liquids 1,2-Dimethyl-3-butylimidazolium bis(trifluoromethanesulfonimide) $[\text{BMMIM}]\text{NTf}_2^1$, 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) $[\text{BMIM}]\text{NTf}_2^1$, 1-*n*-Decyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) $[\text{C}_{10}\text{MMIM}]\text{NTf}_2^{1,2}$, 1-(2,3-Dihydroxypropyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) $[\text{C}_1\text{C}_1(\text{EG})\text{IM}]\text{NTf}_2^3$, 1-*n*-Butyronitrile-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) $[\text{CNC}_3\text{MMIM}]\text{NTf}_2^{1,4}$ and 1-*n*-Butyronitrile-3-methylimidazolium bis(trifluoromethanesulfonimide) $[\text{CNC}_3\text{MIM}]\text{NTf}_2^{1,4}$ were prepared according to known literature methods and were dried in vacuo before they were placed in the glove box. All other commercially available chemicals were used without further purification.

Analytical methods

Transmission electron spectroscopy was recorded on Zeiss LEO912 with 120 kV. For the sample preparation one drop of the NP-dispersion embedded in ionic liquid was diluted in 2 ml acetone. Of this solution one drop was placed onto a holey carbon-coated copper grid.

^1H -, ^{13}C -APT- and ^{19}F -NMR spectroscopy were recorded on a *Bruker AVANCE II* spectrometer at 298 K (300 MHz, 75 MHz, 182 MHz).

Gas Chromatography with Mass Spectrometry (GC-MS) and Gas Chromatography with Flame Ionization Detector (GC-FID) were performed using Agilent 5973 Network Mass Selective Detector with injection, auto sample, mass detector and flame ionization detector. As column MN Optima 5 MS Accent was used. As standard temperature program 50-300.MF was used (50 °C (2.0 min, 25 °C/min → 300 °C (5 min) with 0.7 bar and a flow rate of 1.7 ml/min). The yields of (*E*)-stilbene were determined using GC-FID.

Synthesis of Ni-NPs

In a typical experiment, adapted to our previous protocol,⁵ a screw-capped vial with butyl/PTFE septum was loaded with [Ni(COD)₂] (10.5 mg, 0.038 mmol) and the appropriate ionic liquid (0.15 g) under argon. The suspension was heated to 70 °C and stirred under argon for 20 h resulting in a black suspension. The NP-suspension was evaporated under reduced pressure to remove volatile by-products from the decomposition of the organometallic precursor. The monometallic Ni-NPs in [C₁C₁(EG)IM]NTf₂ were prepared according a literature method.⁶

Hydrogenation reaction

In a typical experiment to the freshly prepared Ni-NPs in IL was added 0.76 mmol of the alkyne with 0.5-1.0 ml cyclohexane as co-solvent. Then the vial was placed in a stainless steel autoclave, the reactor was sealed, charged with 1 or 4 bar H₂ and was placed into a preheated aluminium heating block (1000 rpm) at the appropriate temperature. After the appropriate reaction time the reactor was cooled down to room temperature. For the work-up procedure the reaction mixture was extracted with 5 x 2 ml *n*-pentane, the solvent was evaporated under reduced pressure and 20 µl (0.01 mmol) hexamethyldisilane as internal standard was added. Alternatively for more volatile compounds, cyclohexane was used as internal standard. The residue was analysed using ¹H- and ¹³C-APT-NMR spectroscopy and was compared to literature data.

For recycling experiments the solvent residues after the work up procedure were removed under reduced pressure. Afterwards new substrate and co-solvent was added and the reaction mixture was hydrogenated using the standard reaction conditions.

Test reaction without catalyst or applied H₂ pressure

Table 1: Hydrogenation of diphenylacetylene without Ni-catalyst and without applied H₂ pressure. 2: (Z)-stilbene, 3: (E)-stilbene, 4: 1,2-diphenylethane.

Entry	Ni-NPs in [CNC ₃ MMIM]NTf ₂ [mol%]	pH ₂ [bar]	Conv. [%]	2	3	4
1 ^a	-	4	0	0	0	0
2	5 mol%	-	0	0	0	0

Reaction conditions: 30 °C, 16 h, 1 ml cyclohexane. ^a0.15 g [CNC₃MMIM]NTf₂ was added to the reaction mixture.

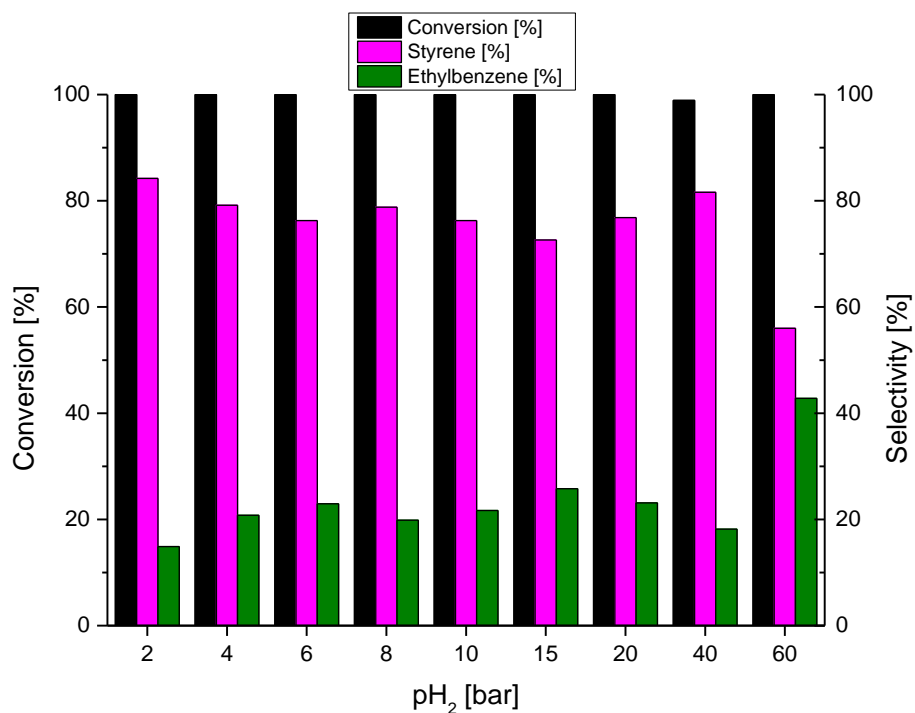
Hydrogenation reaction with additive

Table 2: Hydrogenation of diphenylacetylene with Ni-NPs in [BMMIM]NTf₂ and acetonitrile as additive. 2: (Z)-stilbene, 3: (E)-stilbene, 4: 1,2-diphenylethane.

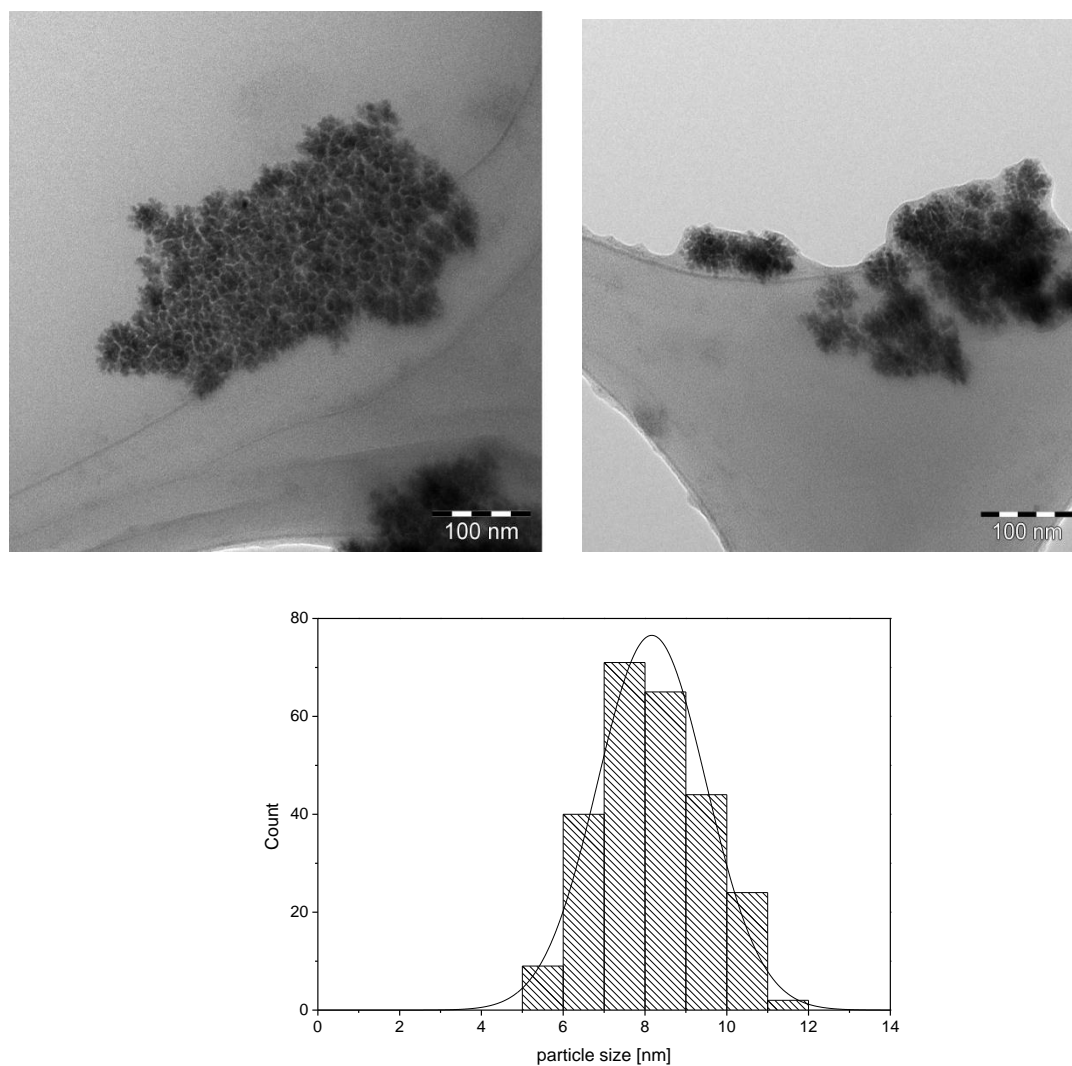
Entry	Me-CN [eq.]	Conv. [%]	2	3	4
1	0.5	100	90.3	2.6	6.7

The synthesis of the Ni-NPs was conducted in 0.15 g [BMMIM]NTf₂. Reaction conditions of the hydrogenation reaction: 30 °C, 4 bar H₂, 16 h, 1 ml cyclohexane.

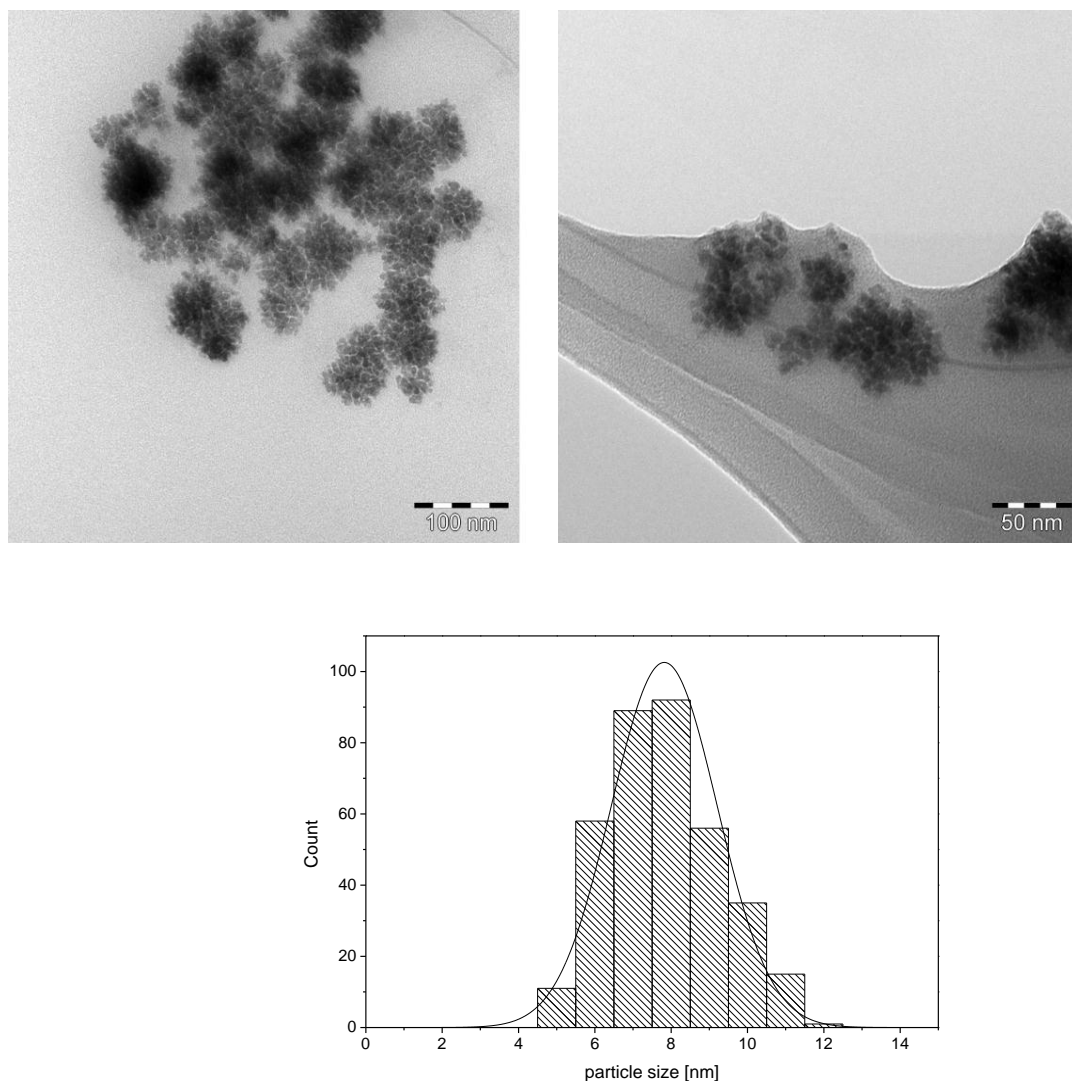
H₂ Pressure variation



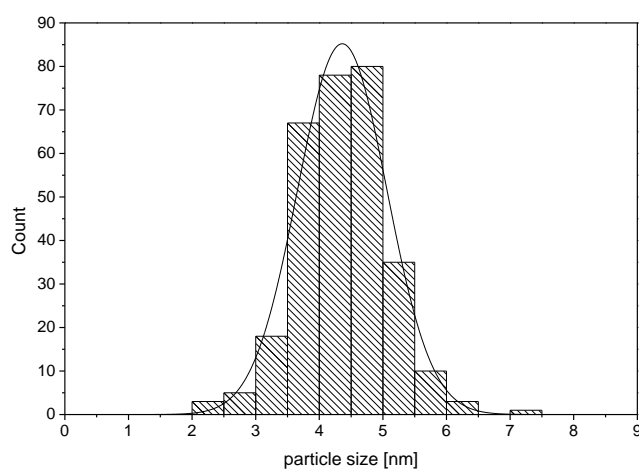
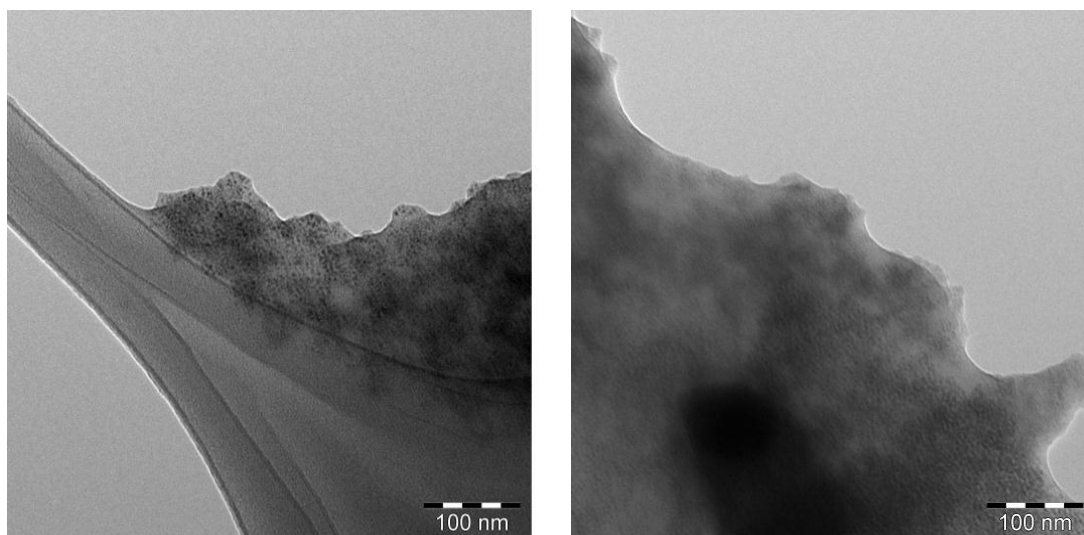
SI-Figure 1: Hydrogenation of phenylacetylene with Ni-NPs in [CNC₃MMIM]NTf₂ under varying H₂ pressure. Reaction condition of the hydrogenation reactions: 30 °C, 2-60 bar H₂, 3 h, cyclohexane. The H₂ pressure variation for the hydrogenation of phenylacetylene provided that 100% conversion with selectivity for the styrene of about 73-84% can be obtained within 3 h at H₂ pressures between 2-40 bar. At 1 bar H₂ pressure 100% conversion has been obtained only after 16 h (7 h: 62%). Contrary at pressures as high as 60 bar H₂, the selectivity for styrene drops significantly down to 56%. This shows that already low H₂ pressures (<5 bar) are sufficient for high conversion and selectivity and this reflects the very high activity of the Ni-nanoscale catalyst in contrast to our previous reported iron based system.

Catalyst characterisation

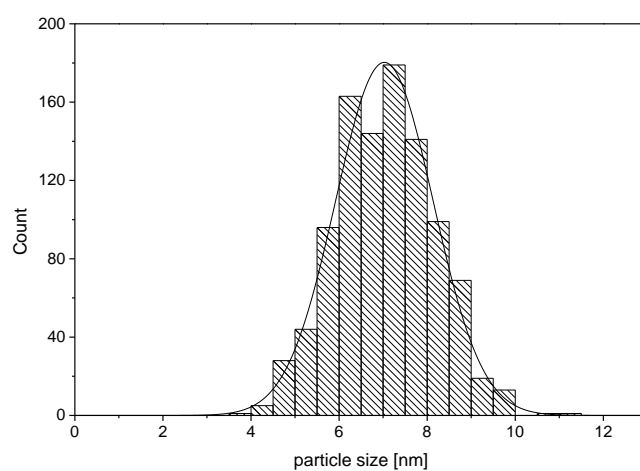
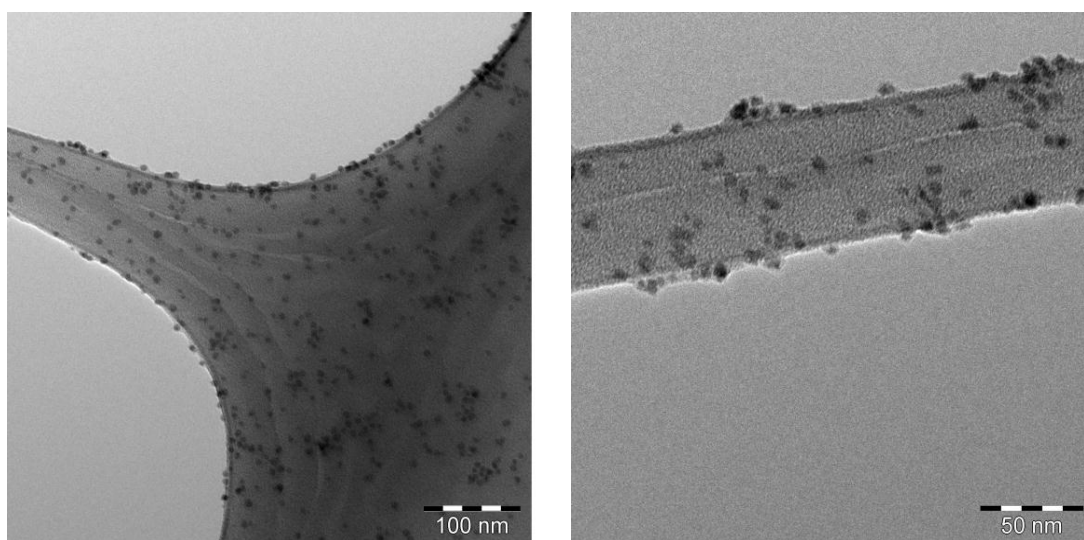
SI-Figure 2: TEM picture of Ni-NPs dispersed in [BMIM]NTf₂ (38 μ mol metal in 0.3 g IL, 70 $^{\circ}$ C, 20 h) and histogram of size distribution. The mean particle diameter is 8.2 ± 1.3 nm.



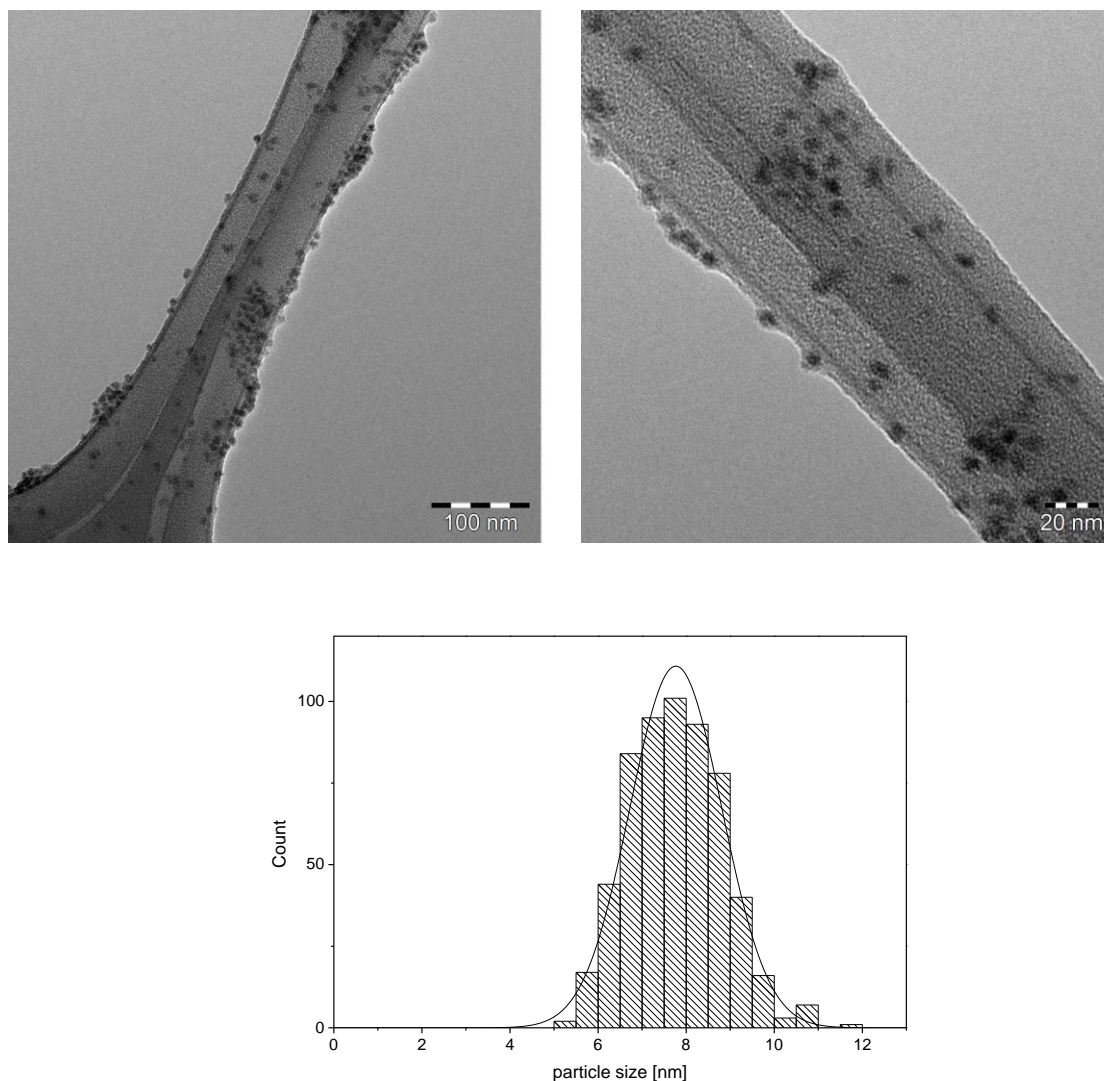
SI-Figure 3: TEM picture of Ni-NPs dispersed in [BMMIM]NTf₂ (38 μ mol metal in 0.3 g IL, 70 $^{\circ}$ C, 20 h) and histogram of size distribution. The mean particle diameter is 7.8 ± 1.4 nm.



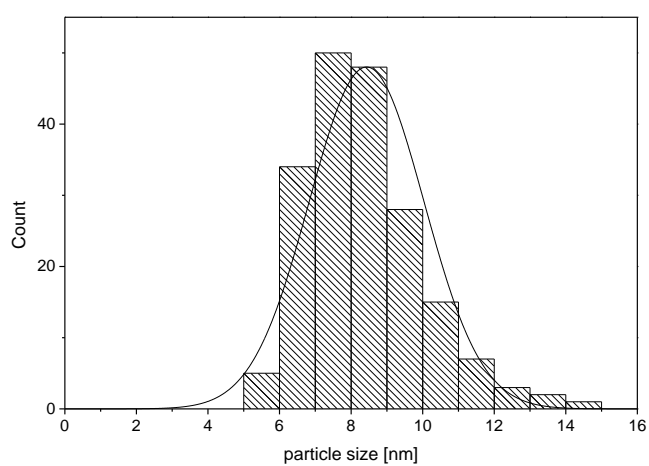
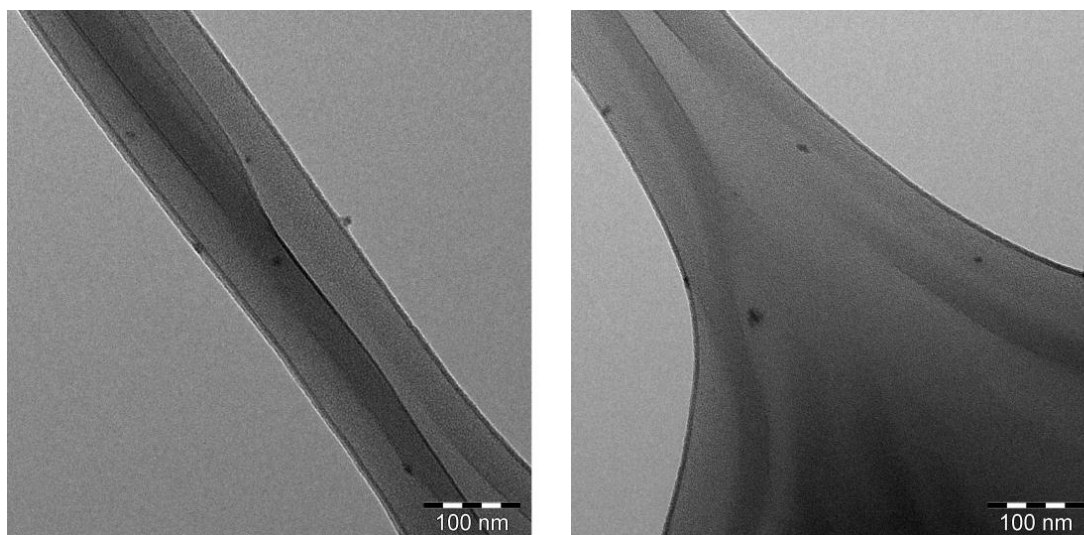
SI-Figure 4: TEM picture of Ni-NPs dispersed in $[C_{10}MMIM]NTf_2$ (38 μ mol metal in 0.3 g IL, 70 $^{\circ}$ C, 20 h) and histogram of size distribution. The mean particle diameter is 4.4 ± 0.7 nm.



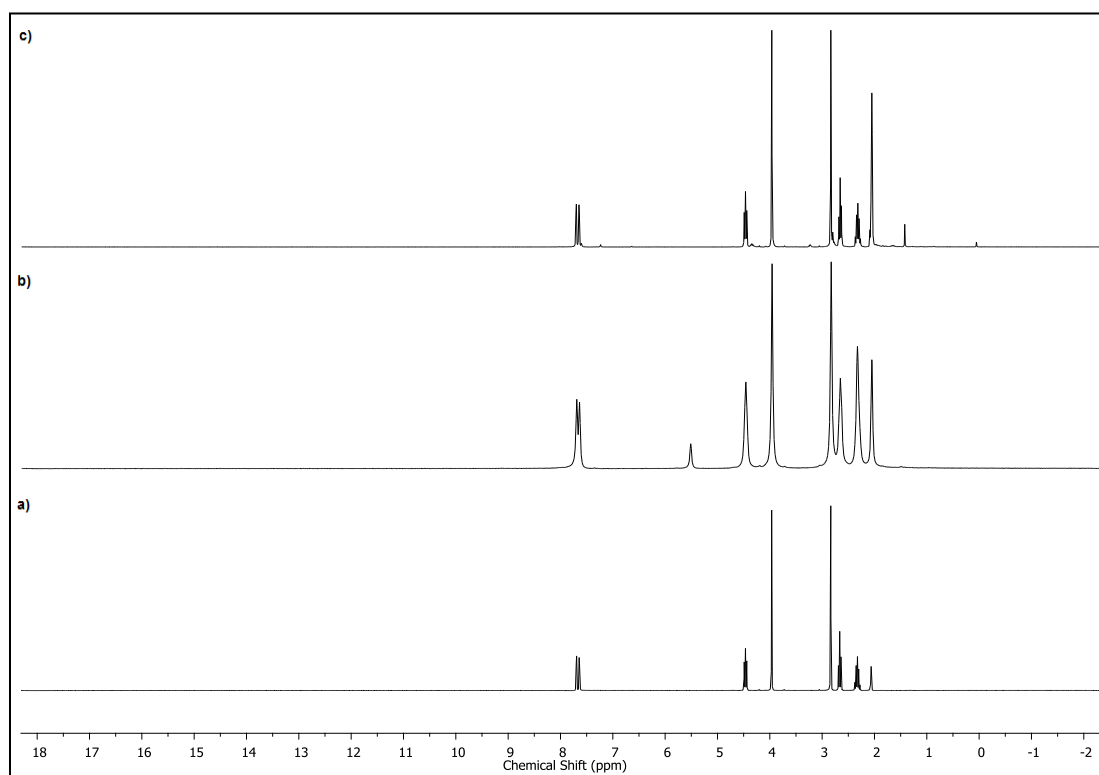
SI-Figure 5: TEM picture of Ni-NPs dispersed in $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ (38 μmol metal in 0.3 g IL, 70 $^\circ\text{C}$, 20 h) and histogram of size distribution. The mean particle diameter is 7.0 ± 1.1 nm.



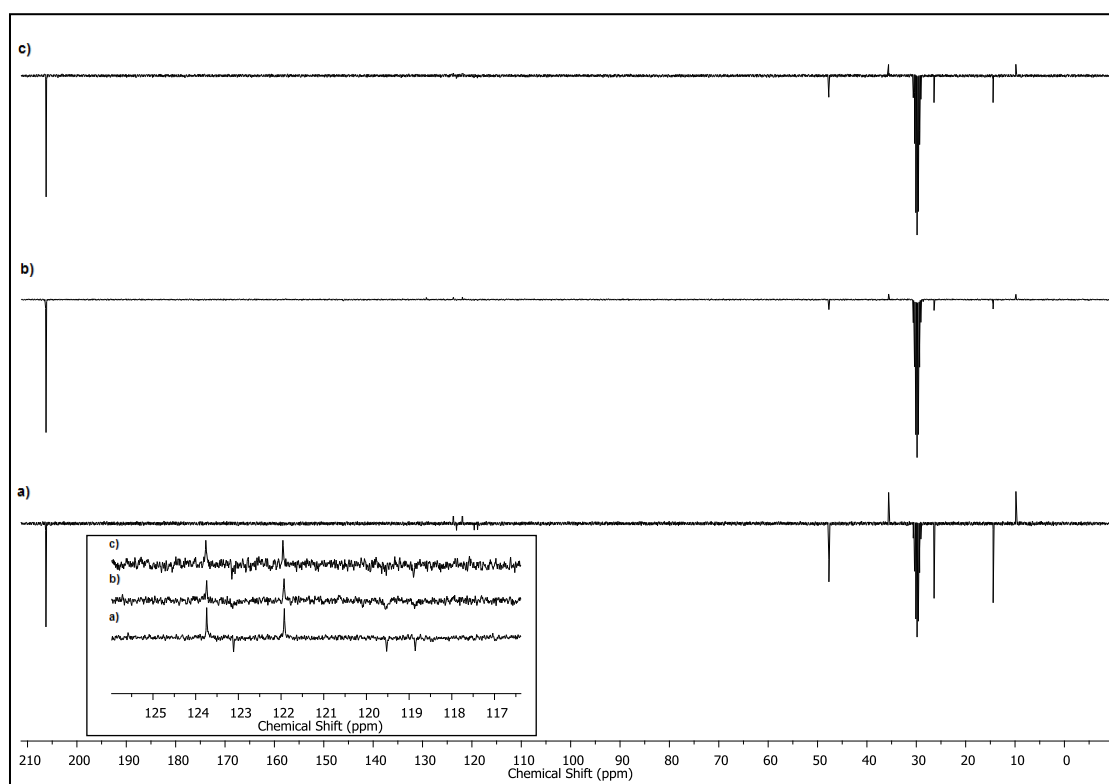
SI-Figure 6: TEM picture of Ni-NPs dispersed in $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ (38 μmol metal in 0.15 g IL, 70 $^\circ\text{C}$, 20 h) and histogram of size distribution. The mean particle diameter is 7.8 ± 1.1 nm.



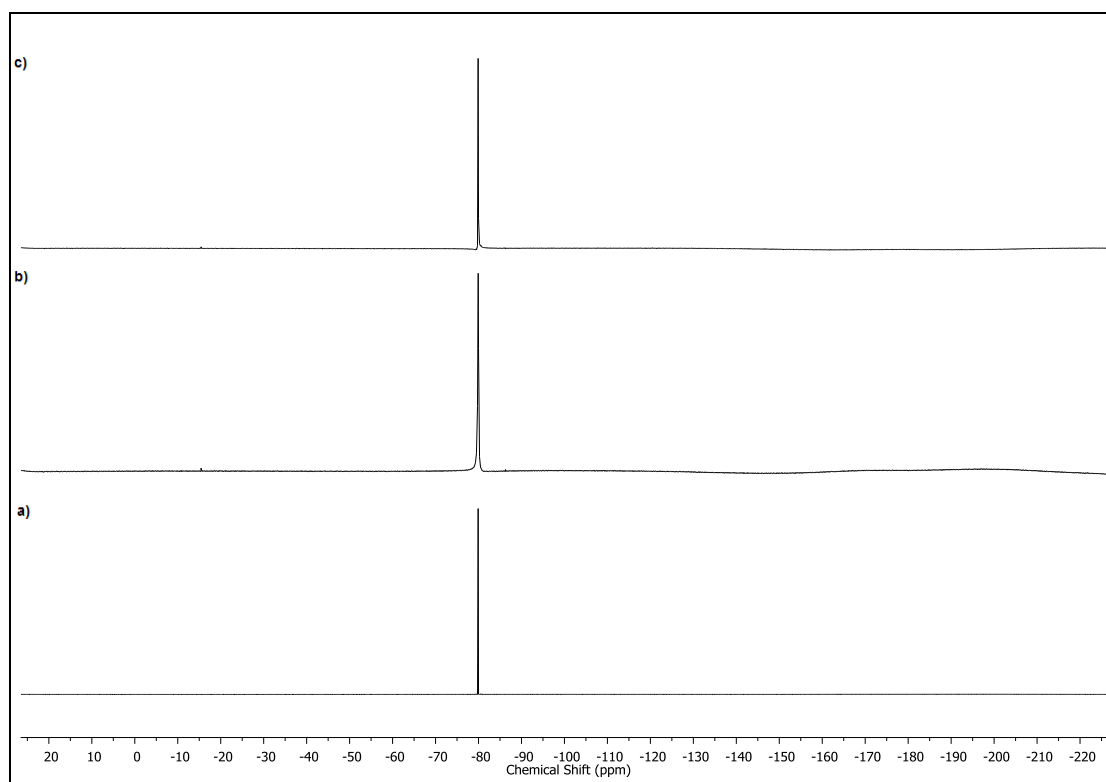
SI-Figure 7: TEM picture of Ni-NPs dispersed in [CNC₃MIM]NTf₂ (38 μ mol metal in 0.15 g IL, 70 $^{\circ}$ C, 20 h) and histogram of size distribution. The mean particle diameter is 8.4 ± 1.6 nm.

NMR spectra of the ionic liquid $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ 

SI-Figure 8: ^1H -NMR (300 MHz, Acetone- d_6) of the $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ phase of a) pure IL, b) after the synthesis of Ni-NPs, c) after the hydrogenation reaction of diphenylacetylene (30 °C, 4 bar H_2 , 16 h).



SI-Figure 9: ^{13}C -APT-NMR (75 MHz, Acetone- d_6) of the $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ phase of a) pure IL, b) after the synthesis of Ni-NPs, c) after the hydrogenation reaction of diphenylacetylene (30 °C, 4 bar H_2 , 16 h).



SI-Figure 10: ^{19}F -NMR (282 MHz, Acetone- d_6) of the $[\text{CNC}_3\text{MMIM}]\text{NTf}_2$ phase of a) pure IL, b) after the synthesis of Ni-NPs, c) after the hydrogenation reaction of diphenylacetylene (30 °C, 4 bar H_2 , 16 h).

Determination of active catalyst surface and turn over number (TON)

The active catalyst surface was determined using the magical number approach considering Ni(0)-NPs in a zero oxidation state with a spherical and an approximately icosahedron shape of the nanoparticles. Using equations (1) and (2)⁷ with N_A as the Avogadro number with $6.02214 \cdot 10^{23}$, ρ as the density of nickel with 8.908 g/cm³, A_r as the weight of one nickel atom with 58.6934 g/mol and D as mean the particle diameter of 7.8 ± 1.1 nm determined by TEM analysis the Volume of one nickel particle was determined to be 248 nm³. This results in approximately 22710 atoms per nickel particle.

$$N = \frac{N_A \cdot \rho \cdot V}{A_r} \quad (1)$$

$$V = \frac{4}{3} \pi \cdot \left(\frac{D}{2}\right)^3 \quad (2)$$

$$G_n = \frac{1}{3}(2n + 1) \cdot (5n^2 + 5n + 3) \quad (3)$$

$$S_n = 10n^2 + 2 \quad (4)$$

Using equation (3) and (4) by *Teo* and *Sloane*⁸ with G_n as the total number of particles and S_n as the number of surface particles, the number of shells n for the synthesised nickel nanoparticle is about 18 which leads to a 14.3 % atoms on the surface of the nickel nanoparticle. These surface atoms are considered as the active species in heterogeneous catalysed reactions. The turn over number (TON) was calculated using equation (5) with n as amount of product and catalyst surface respectively.

$$TON = \frac{n_{product}}{n_{catalyst\ surface}} \quad (5)$$

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