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Nitrile hydrogenation using nickel nanocatalysts in ionic liquids

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Experimental

General methods

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

The chemicals benzonitrile, 2-aminobenzonitrile, hepytl cyanide and mesitylene were purchased from *SigmaAldrich.* 4-Bromobenzonitrile and 4-cyanobenzoic acid were purchased from *ABCR. p*-Tolunitrile, 4-chlorobutyronitrile and bis(1,5-cyclooctadiene)nickel(0) were purchased from *Acros Organics*. 4-Iodobenzonitrile was purchased from *Alfa Aesar* and 4-propoxybenzonitrile was purchased from *Maybridge*. 1,4-Dioxane was purchased from *VWR*.

The ionic liquids 1,2-dimethyl-3-butylimidazolium bis(trifluoromethanesulfonimide) [BMMIM]NTf$_2$[1], 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [BMIM]NTf$_2$[1], 1-*n*-decyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) [C$_{10}$MMIM]NTf$_2$[1, 2], 1-(3-Cyanopropyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) [CNC$_3$MMIM]NTf$_2$[1, 3] and 1-(3-Cyanopropyl)-3-methylimidazolium bis(trifluoromethanesulfonimide) [CNC$_3$MIM]NTf$_2$[1, 3] were prepared according to known literature procedures. All ionic liquids 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 microscopy (TEM) was recorded on Zeiss LEO912 with 120 kV. Samples were prepared by dilution of the NP-dispersion embedded in ionic liquid in few millilitres acetone. One drop of this solution was placed onto a holey carbon-coated copper grid.

^{1}H-, ^{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).

Experimental part

Synthesis of Ni-NPs

In a typical experiment, adapted to our previous protocol,[4, 5] a screw-top vial with butyl/PTFE septum was loaded with [Ni(COD)$_2$] (10.5 mg, 0.038 mmol) and the IL [BMMIM]NTf$_2$ (0.3 g) under argon. The suspension was heated to 70 °C and stirred (500 rpm) under argon for 20 h resulting in a black suspension.

Hydrogenation reactions

In a typical experiment to the freshly prepared NPs-IL dispersion was added 5.23 mmol of the substrate with 0.5 ml mesitylene or 1,4-dioxane as co-solvent. Then the vial was placed in a stainless steel autoclave, the reactor was sealed, charged with hydrogen pressure and was placed into a preheated aluminium heating block 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 or diethyl ether, the solvent was evaporated under reduced pressure and 20 µl (0.01 mmol) hexamethyldisilane as internal standard was added. The residue was analysed using ^{1}H- and ^{13}C-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. Then new substrate was added and the reaction mixture was hydrogenated using the standard reaction conditions.

NMR analysis of the ionic liquids

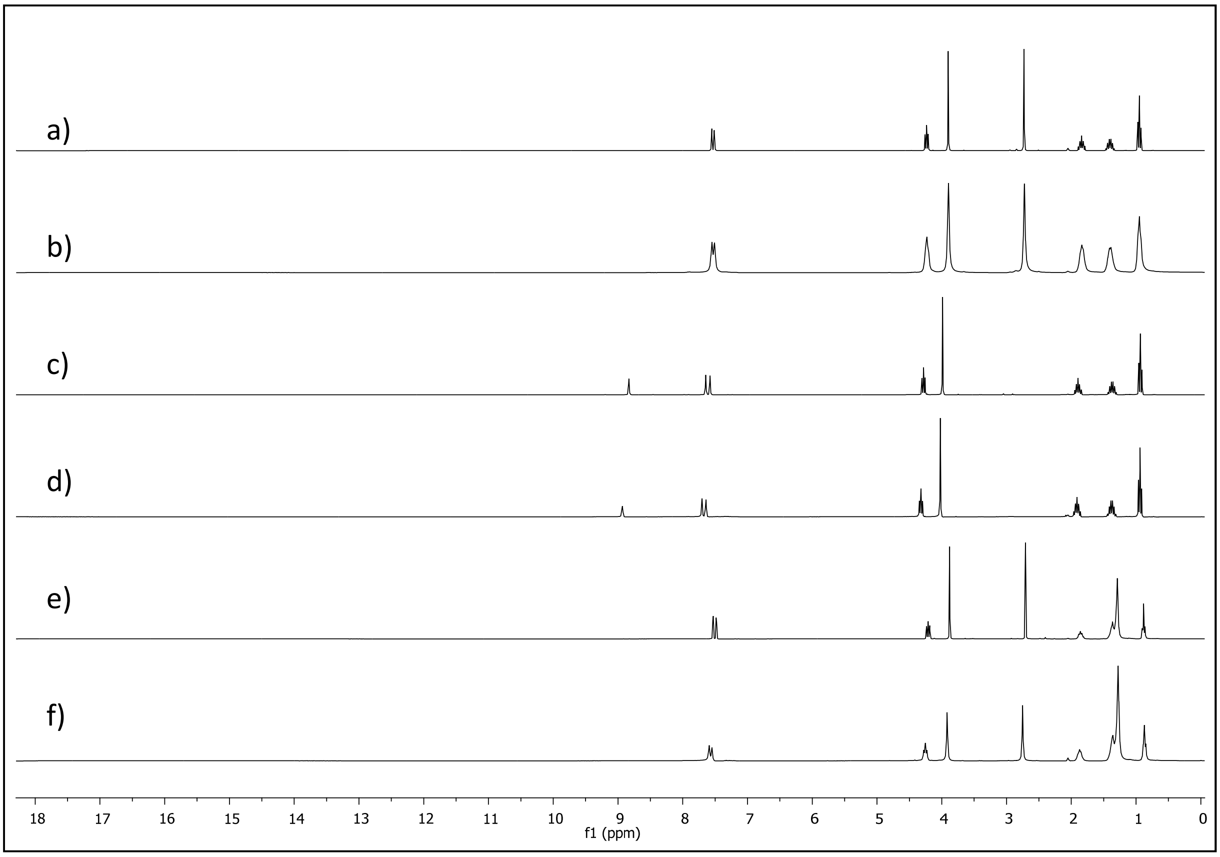

Figure S 1: ^{1}H NMR spectra of a) [BMMIM]NTf$_2$, b) [BMMIM]NTf$_2$ after catalysis, c) [BMIM]NTf$_2$, d) [BMIM]NTf$_2$ after catalysis, e) [C$_{10}$MMIM]NTf$_2$ and f) [C$_{10}$MMIM]NTf$_2$ after catalysis. Reaction conditions of catalysis reaction: hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor, 90 °C, 25 bar H$_2$, 22 h.

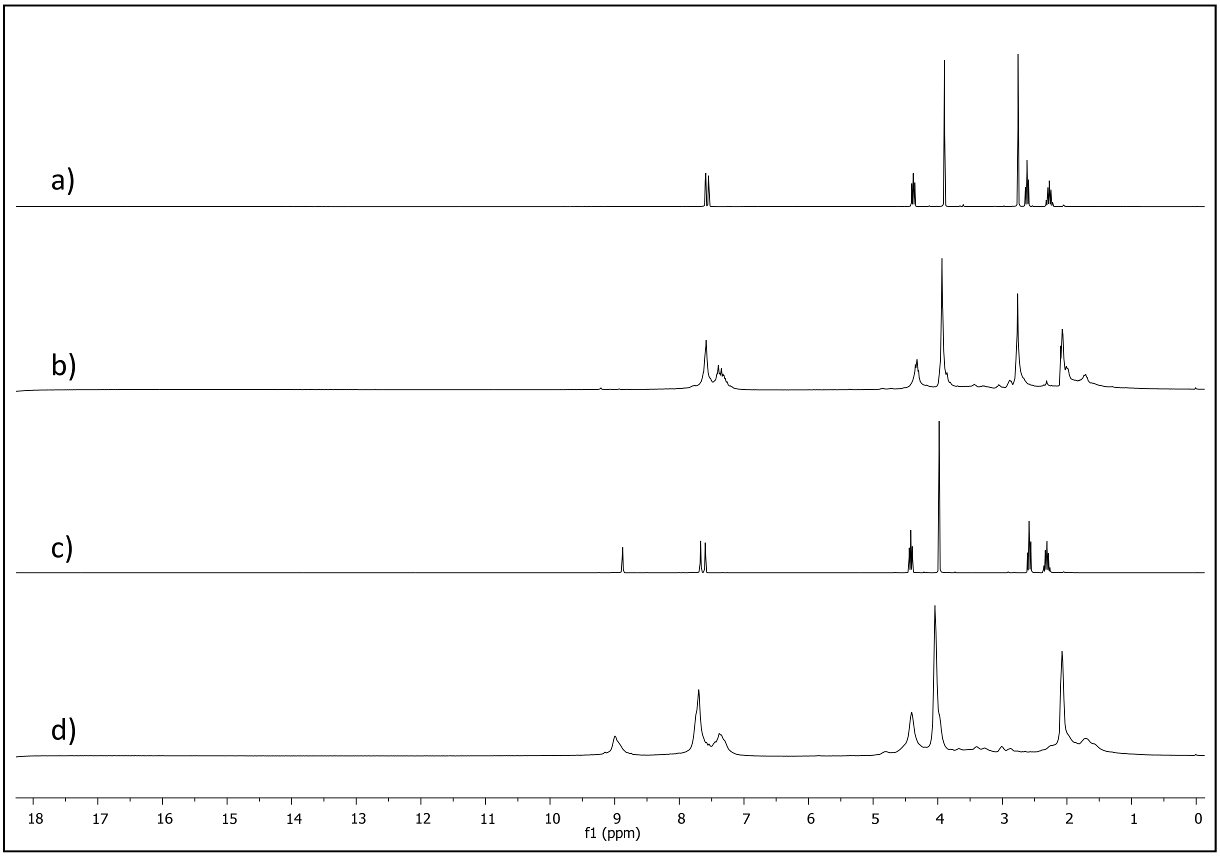

Figure S 2:^{1}H NMR spectra of a) [CNC$_3$MMIM]NTf$_2$, b) [CNC$_3$MMIM]NTf$_2$ after catalysis, c) [CNC$_3$MIM]NTf$_2$ and d) [CNC$_3$MIM]NTf$_2$ after catalysis. Reaction conditions of catalysis reaction: hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H$_2$, 22 h.

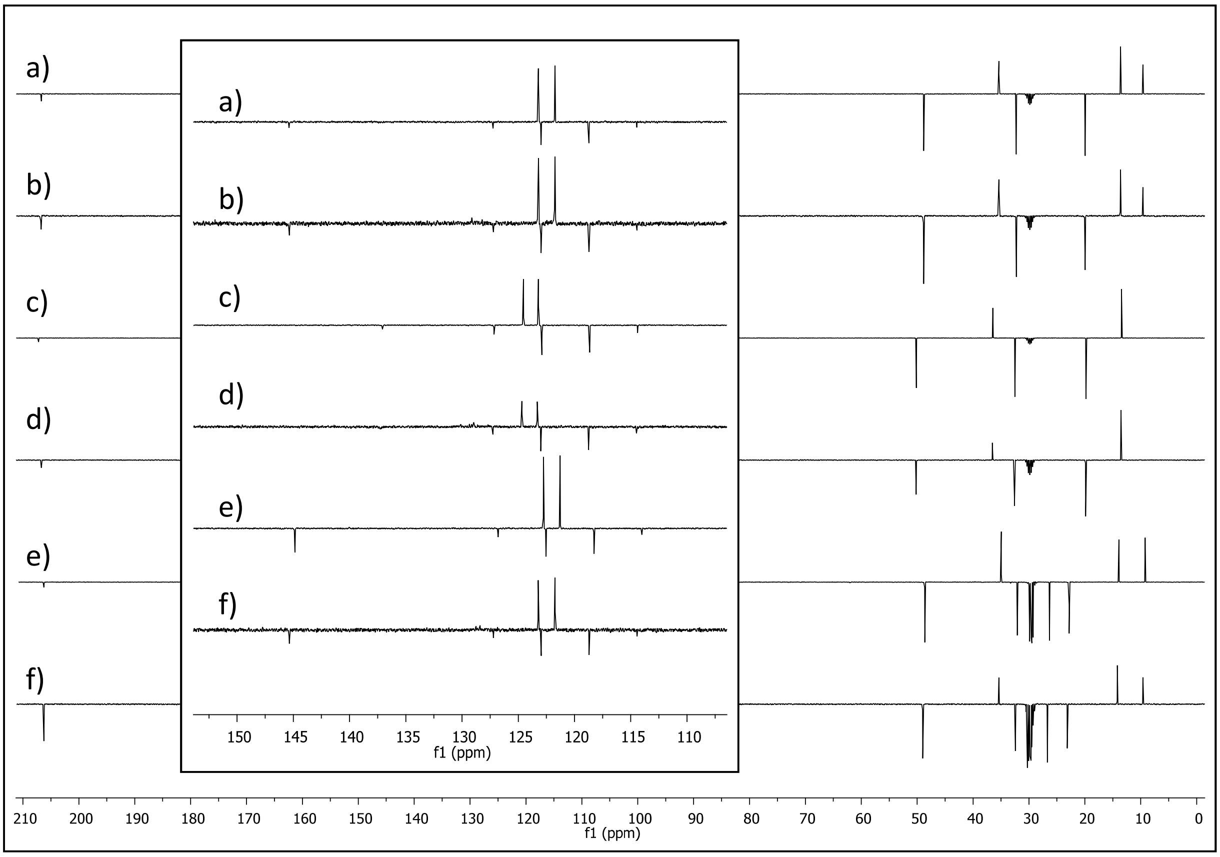

Figure S 3: ^{13}C NMR spectra of a) [BMMIM]NTf$_2$, b) [BMMIM]NTf$_2$ after catalysis, c) [BMIM]NTf$_2$, d) [BMIM]NTf$_2$ after catalysis, e) [C$_{10}$MMIM]NTf$_2$, f) [C$_{10}$MMIM]NTf$_2$ after catalysis, Reaction conditions of catalysis reaction: hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H$_2$, 22 h.

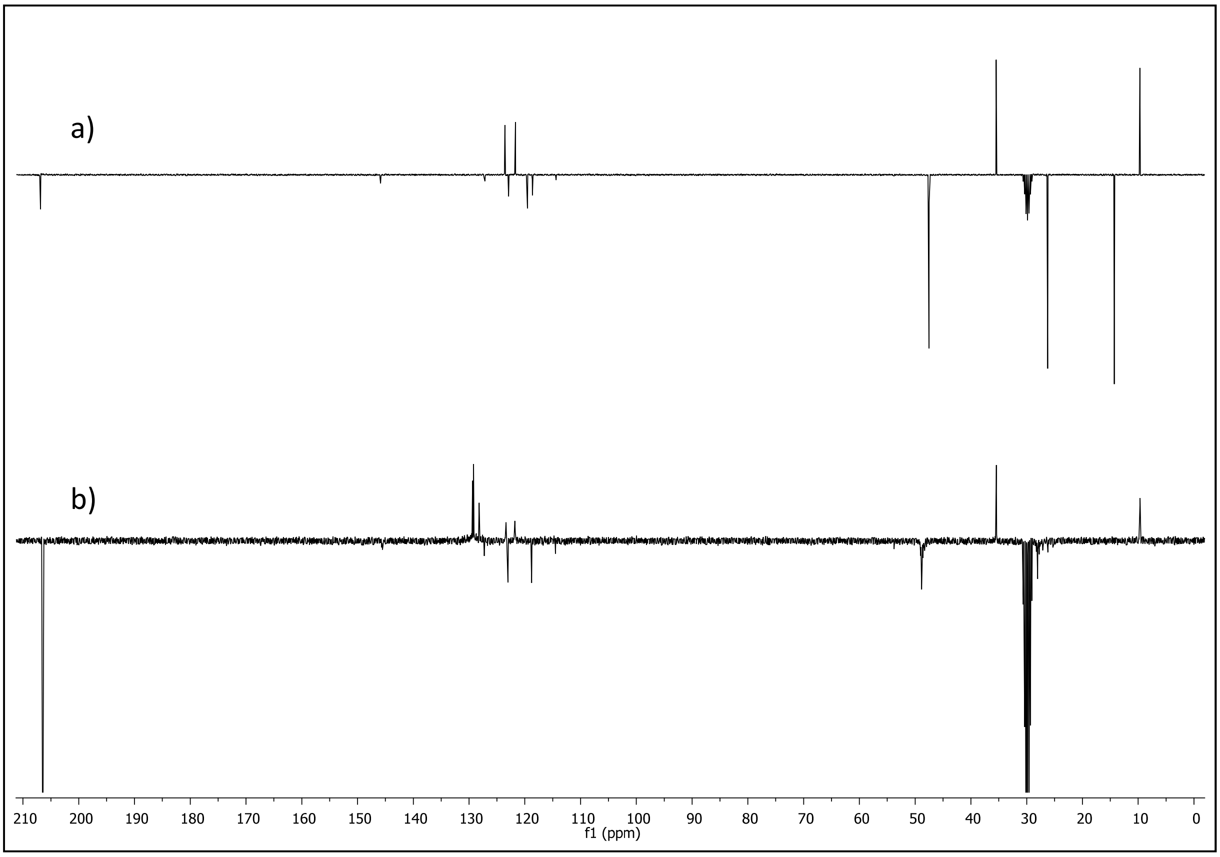

Figure S 4: ^{13}C NMR spectra of a) [CNC$_3$MMIM]NTf$_2$ and b) [CNC$_3$MMIM]NTf$_2$ after catalysis. Reaction conditions of catalysis reaction: Hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H_2, 22 h.

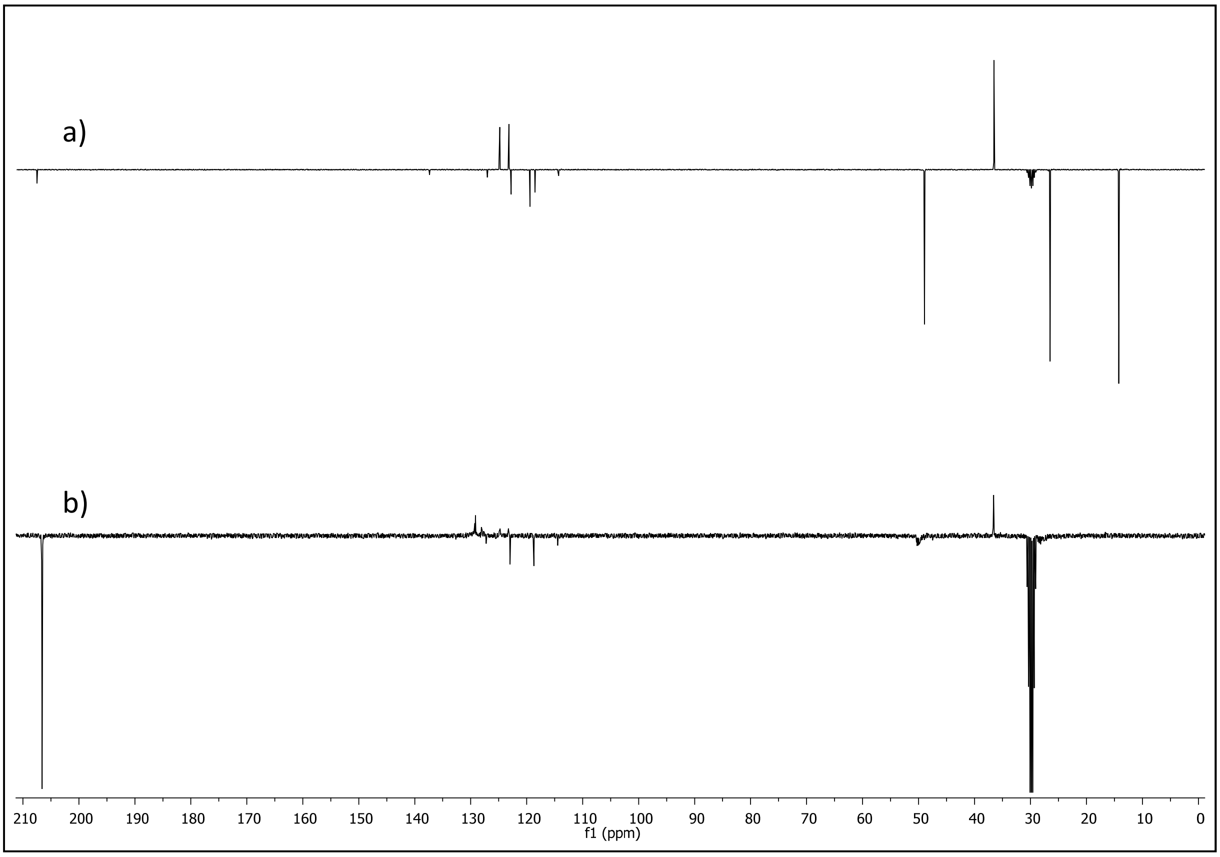

Figure S 5: ^{13}C NMR spectra of a) [CNC$_3$MIM]NTf$_2$ and b) [CNC$_3$MIM]NTf$_2$ after catalysis. Reaction conditions of catalysis reaction: Hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H$_2$, 22 h.

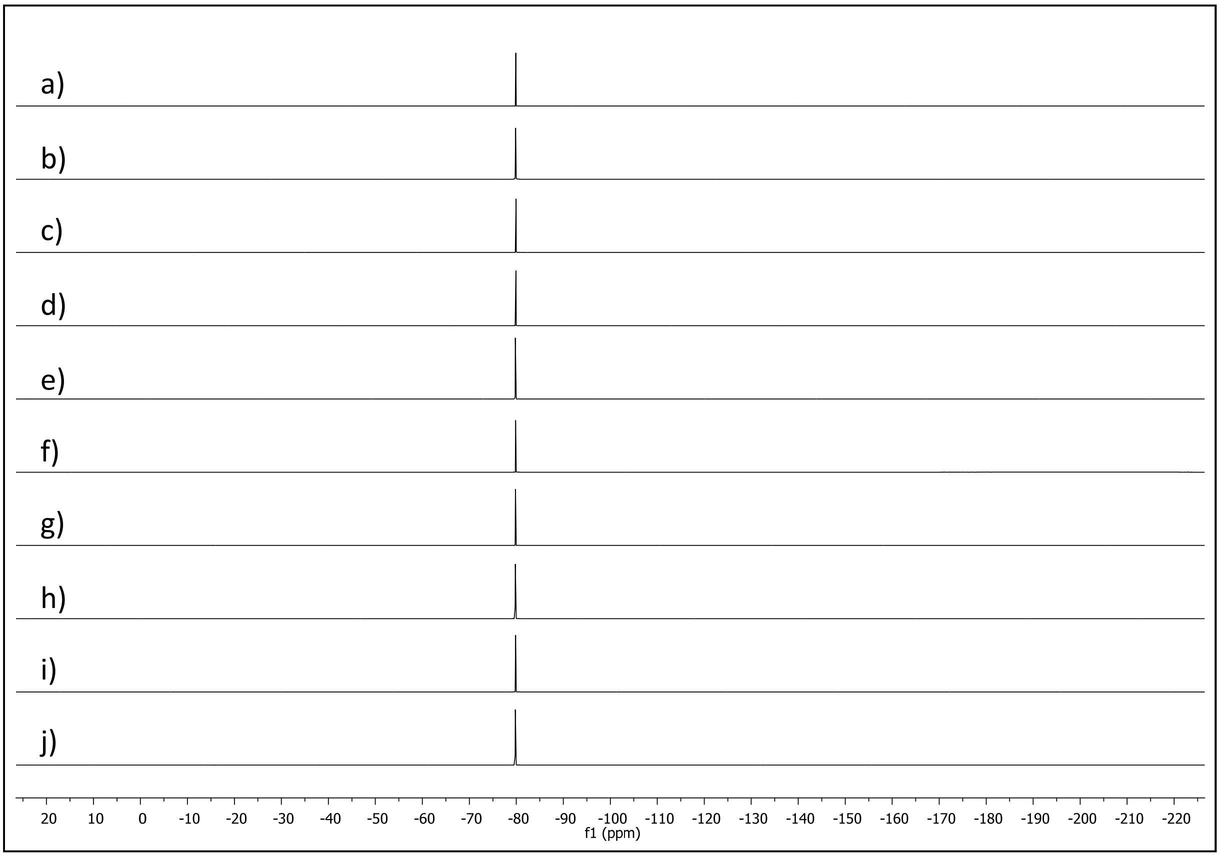

Figure S 6: ^{19}F NMR spectra of a) [BMMIM]NTf$_2$, b) [BMMIM]NTf$_2$ after catalysis, c) [BMIM]NTf$_2$, d) [BMIM]NTf$_2$ after catalysis, e) [C$_{10}$MMIM]NTf$_2$, f) [C$_{10}$MMIM]NTf$_2$ after catalysis, g) [CNC$_3$MMIM]NTf$_2$, h) [CNC$_3$MMIM]NTf$_2$ after catalysis, i) [CNC$_3$MIM]NTf$_2$ and j) [CNC$_3$MIM]NTf$_2$ after catalysis. Reaction conditions of catalysis reaction: Hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H$_2$, 22 h.

Optimisation reactions with benzonitrile

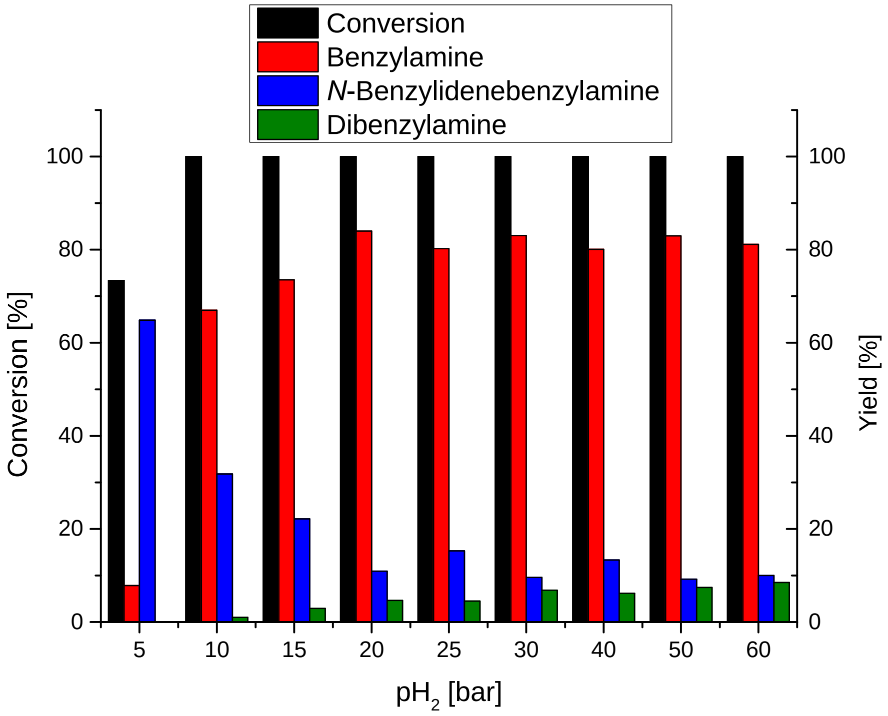

Figure S 7: H_2 pressure screening of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf$_2$. Reaction conditions: 0.7 mol% cat. based on Ni precursor, 90 °C, 22 h.

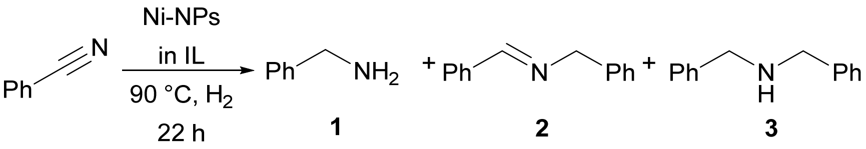

Table S 1: Variation of the temperature and addition of co-solvent on the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf$_2$. Reaction condition: 0.7 mol% based on Ni precursor, 25 bar H_2, 0.5 ml co-solvent. Products: **1**: benzylamine, **2**: *N*-benzylidenebenzylamine, **3**: dibenzylamine.

Entry	**T [°C]**	**Cosolvent**	**Conv. [%]**	**Yield [%]**		
				1	**2**	**3**
1	70	-	94	25	67	<1
2	90	-	100	80	15	5
3	90	mesitylene	100	75	19	4
4	90	1,4-dioxane	100	77	20	3

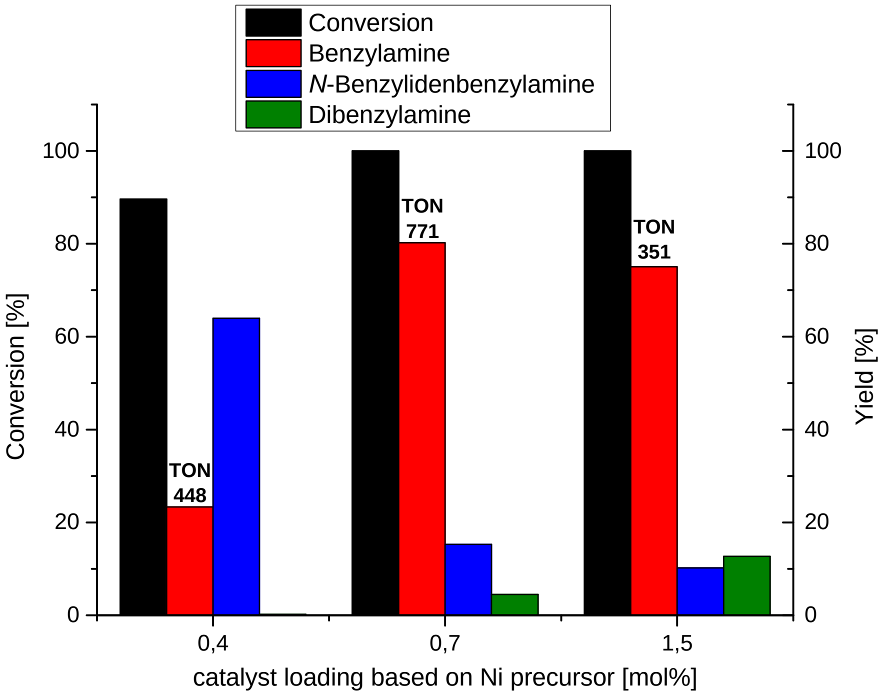

Figure S 8: Conversion and yields of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf$_2$ as a function of the catalyst loading. The hydrogenation reaction without Ni catalyst leads to no conversion. Reaction condition: 90 °C, 25 bar H_2, 22 h.

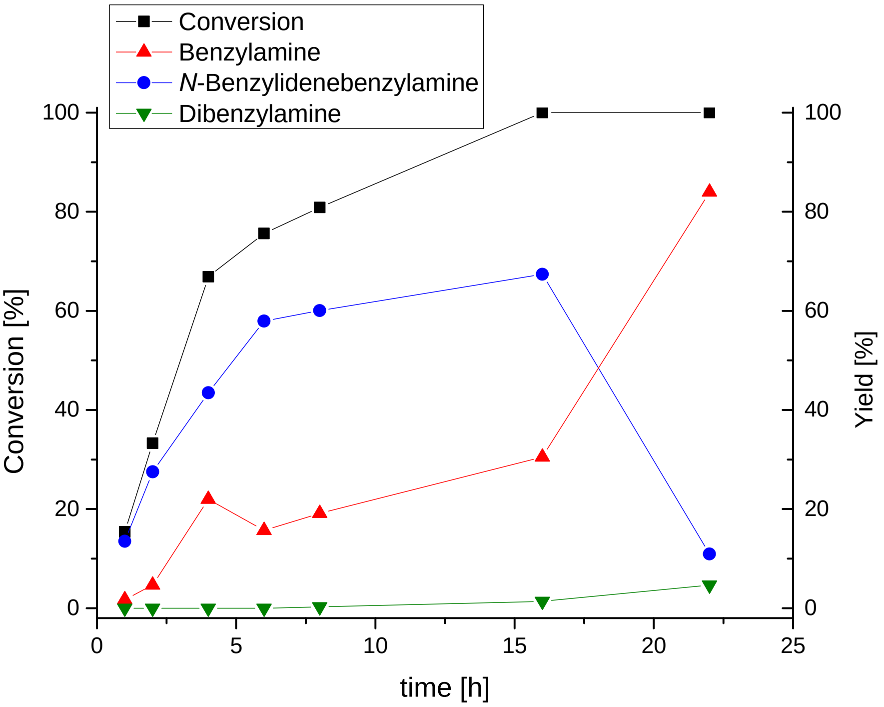

Figure S 9: Time depended reaction course of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf$_2$. Lines are given just for visualisation. Reaction conditions: 0.7 mol% based on Ni precursor, 90 °C, 20 bar H_2.

Catalyst characterisation after recycling experiments

Transmission electron microscopy (TEM) measurement was performed after the recycling experiments of benzonitrile over Ni-NPs in [BMMIM]NTf$_2$. Reaction conditions: 1.4 mol% based on Ni-precursor, 90 °C, 20 bar H$_2$, 22 h. The TEM measurement shows the particle size after the 5th run.

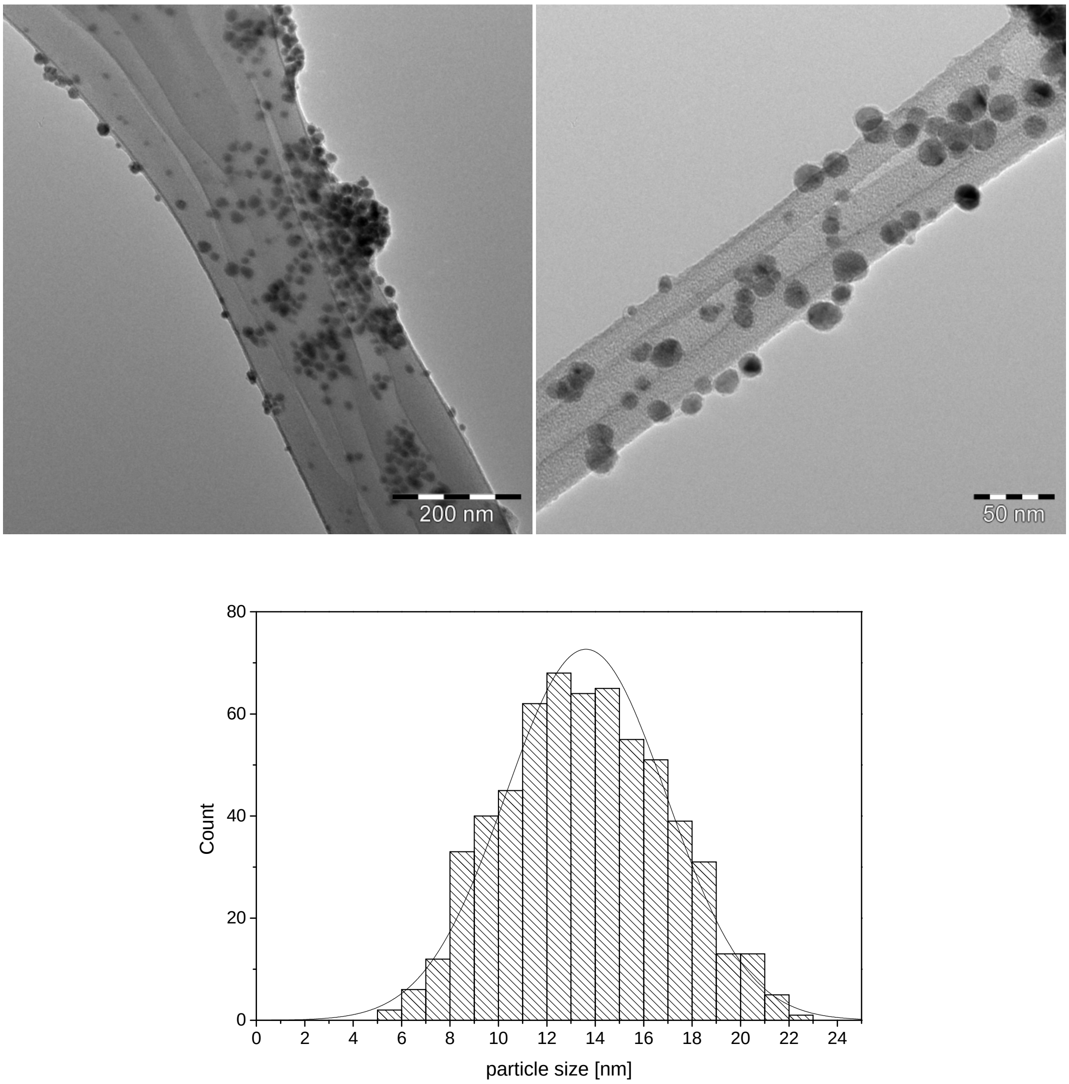

Figure S 10: TEM picture of Ni-NPs dispersed in [BMMIM]NTf$_2$ after the 5th run of recycling experiments of the hydrogenation of benzonitrile (1.4 mol% based on Ni-precursor, 90 °C, 20 bar H$_2$, 22 h) and histogram of size distribution. The mean particle diameter is 13.6 ± 3.3 nm.

Active catalyst surface and turn over number (TON)

The active catalyst surface was calculated by an approach of Teo and Sloane[6]. The Ni(0)-NPs were considered to have a spherical and approximately icosahedrons shape.

(1)[7] $$N = \frac{N_A \cdot \rho \cdot V}{A_r}$$

(2)[7] $$V = \frac{4}{3}\pi \cdot \left(\frac{D}{2}\right)^3$$

(3)[6] $$G_n = \frac{1}{3}(2n+1) \cdot (5n^2 + 5n + 3)$$

(4)[6] $$S_n = 10n^2 + 2$$

(5)[7] $$TON = \frac{n_{product}}{n_{catalyst\ surface}}$$

By the use of equitation (1) and (2) (Avogadro number N_A = 6.02214·10^{23}, density of nickel ρ = 8.908 g/cm^3, weight of one nickel atom A_r = 58.6934 g/mol and D as mean particle diameter of the nickel particles in the appropriate IL[5]) the volume V of one nickel particle and N as the number of Ni atoms per nanoparticle was determined. With equation (3) and (4) using G_n as total number of particles and S_n as number of surface particles, the number of shells n for the nickel nanoparticles can be determined and thus the percentage of atoms on the surface of the nickel nanoparticles. Results obtained from the calculations are given in the following. [BMMIM]NTf$_2$ with D = 7.8±1.4 nm, V = 248 nm³, N = 22710, n = 18 leads to 14.3 % surface atoms. [BMIM]NTf$_2$ with D = 8.2±1.3 nm, V = 289 nm³, N = 26387, n = 19 leads to 13.7 % surface atoms. [C$_{10}$MMIM]NTf$_2$ with D = 4.4±0.7 nm, V = 45 nm³, N = 4077, n = 10 leads to 24.6 % surface atoms [CNC$_3$MMIM]NTf$_2$ with D = 7.0±1.1 nm, V = 180 nm³, N = 16415, n = 16 leads to 15.6 % surface atoms [CNC$_3$MIM]NTf$_2$ with D = 8.2±1.6 nm, V = 289 nm³, N = 26387, n = 19 leads to 13.7 % surface atoms. The turn over number (TON) is determined by the use of equation (5) with n as amount of product and catalyst surface, respectively.[6, 7]

References

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