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, heptyl 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]NTf₂, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [BMIM]NTf₂, 1-n-decyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) [C₁₀MMIM]NTf₂, 1-(3-Cyanopropyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonimide) [CNC₃MMIM]NTf₂, 1-(3-Cyanopropyl)-3-methylimidazolium bis(trifluoromethanesulfonimide) [CNC₃MIM]NTf₂ 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.

¹H-, ¹³C-APT- and ¹⁹F-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, 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) [CNC₃MMIM]NTf₂ and b) [CNC₃MMIM]NTf₂ after catalysis. Reaction conditions of catalysis reaction: Hydrogenation of benzonitrile, 0.7 mol% based on Ni precursor 90 °C, 25 bar H₂, 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: H₂ pressure screening of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf₂. 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]NTf₂. Reaction condition: 0.7 mol% based on Ni precursor, 25 bar H₂, 0.5 ml co-solvent.

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Figure S 8: Conversion and yields of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf₂ as a function of the catalyst loading. The hydrogenation reaction without Ni catalyst leads to no conversion. Reaction condition: 90 °C, 25 bar H₂, 22 h.

Figure S 9: Time depended reaction course of the hydrogenation of benzonitrile over Ni-NPs in [BMMIM]NTf₂. Lines are given just for visualisation. Reaction conditions: 0.7 mol% based on Ni precursor, 90 °C, 20 bar H₂.
**Catalyst characterisation after recycling experiments**

Transmission electron microscopy (TEM) measurement was performed after the recycling experiments of benzonitrile over Ni-NPs in [BMMIM]NTf₂. Reaction conditions: 1.4 mol% based on Ni-precursor, 90 °C, 20 bar H₂, 22 h. The TEM measurement shows the particle size after the 5th run.

![TEM picture of Ni-NPs dispersed in [BMMIM]NTf₂ after the 5th run of recycling experiments of the hydrogenation of benzonitrile (1.4 mol% based on Ni-precursor, 90 °C, 20 bar H₂, 22 h) and histogram of size distribution. The mean particle diameter is 13.6 ± 3.3 nm.](image)

Figure S 10: TEM picture of Ni-NPs dispersed in [BMMIM]NTf₂ after the 5th run of recycling experiments of the hydrogenation of benzonitrile (1.4 mol% based on Ni-precursor, 90 °C, 20 bar H₂, 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. The Ni(0)-NPs were considered to have a spherical and approximately icosahedrons shape.

\( N = \frac{N_A \cdot \rho \cdot V}{A_r} \)  
\( V = \frac{4}{3} \pi \cdot \left( \frac{D}{2} \right)^3 \)  
\( G_n = \frac{1}{3} (2n + 1) \cdot (5n^2 + 5n + 3) \)  
\( S_n = 10n^2 + 2 \)  
\( TON = \frac{n_{\text{product}}}{n_{\text{catalyst surface}}} \)

By the use of equations (1) and (2) (Avogadro number \( N_A = 6.02214 \cdot 10^{23} \), density of nickel \( \rho = 8.908 \text{ g/cm}^3 \), weight of one nickel atom \( A_r = 58.6934 \text{ g/mol} \) 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 \( D = 7.8 \pm 1.4 \text{ nm} \), \( V = 248 \text{ nm}^3 \), \( N = 22710 \), \( n = 18 \) leads to 14.3 % surface atoms. [BMIM]NTf\(_2\) with \( D = 8.2 \pm 1.3 \text{ nm} \), \( V = 289 \text{ nm}^3 \), \( N = 26387 \), \( n = 19 \) leads to 13.7 % surface atoms. [C\(_{10}\)MMIM]NTf\(_2\) with \( D = 4.4 \pm 0.7 \text{ nm} \), \( V = 45 \text{ nm}^3 \), \( N = 4077 \), \( n = 10 \) leads to 24.6 % surface atoms [CNC\(_3\)MMIM]NTf\(_2\) with \( D = 7.0 \pm 1.1 \text{ nm} \), \( V = 180 \text{ nm}^3 \), \( N = 16415 \), \( n = 16 \) leads to 15.6 % surface atoms [CNC\(_3\)MIM]NTf\(_2\) with \( D = 8.2 \pm 1.6 \text{ nm} \), \( V = 289 \text{ nm}^3 \), \( N = 26387 \), \( n = 19 \) 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