

Supporting Information

Biphasic hydrogenation over PVP stabilized Rh nanoparticles in hydroxyl functionalized ionic liquids

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Experimental

General Method. Preparation of hydroxyl-functionalized ionic liquids, including 1-(2-hydroxyethyl)-3-methyl imidazolium based ILs, 1-(2-hydroxyethyl)-3-methyl pyridinium based ILs, and 1-(2-hydroxyethyl)-1-methyl piperidinium based ILs, were prepared through a classical two step protocol. Rhodium nanoparticles were prepared by reduction in ethanol/water using polyvinylpyrrolidone (PVP) as stabilizer according to a literature method.¹ Analytical rhodium standard solution, sodium tetrafluoroborate, sodium hexafluorophosphate, lithium bis(trifluoromethylsulfonyl)amide, 2-bromoethanol, 3-picoline, N-methylpiperidine and PVP were purchased from Aldrich and used as received. NMR spectra were obtained at 20°C with a Bruker DMX 400 instrument. GC analyses were conducted on a Varian Chrompack CP-3380 equipped with a capillary column (25 m x 0.25 mm, using N₂ as carrier gas). IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. TEM images were obtained on a PHILLIPS CM 20 transmission electron microscope. Elemental analysis of rhodium was carried out on a Perkin-Elmer Optima

2000 ICP-OES spectrometer. Intensities of spectral of all samples and standards were measured at 343.489 nm and analysis repeated three times. The rhodium level in the samples was determined by comparison with the standard of rhodium solutions with known concentrations.

General procedure for synthesis of 3-(2-hydroxyethyl)-1-methyl imidazolium bromide [C₂OHmim]Br, 1-(2-hydroxyethyl)-3-methyl pyridinium bromide [C₂OHmpy]Br and 1-(2-hydroxyethyl)-1-methyl piperidinium bromide [C₂OHmpip]Br

A mixture of 1-methylimidazole (20 ml, 20.6 g) and 2-bromoethanol (20 ml, 35.2 g) was stirred for 2 days at room temperature, during which time precipitation was observed. Diethyl ether (40 ml) was added into the mixture and vigorously stirred for 1 h. The precipitate was removed by filtration, washed with diethyl ether (3 × 40 ml) and the solid dried under vacuum for 24 h. The synthesis of [C₂OHmpy]Br, [C₂OHmpip]Br were conducted in a similar way.

[C₂OHmim]Br: yield: 90% ¹H NMR (D₂O) δ = 8.62 (s, 1H), 7.40 (s, 1H), 7.35 (s, 1H), 4.21 (t, J (H, H) = 4.8 Hz, 2H), 3.80-3.83 (m, 5H).

[C₂OHmpy]Br: yield: 85% ¹H NMR (D₂O) δ = 8.58 (s, 1H), 8.53 (d, J (H, H) = 8.0 Hz, 1H), 8.28 (d, J (H, H) = 8.0 Hz 1H), 7.83 (t, J (H, H) = 8.0 Hz, 1H), 4.55 (t, J (H, H) = 4.8 Hz, 2H), 3.94 (t, J (H, H) = 4.8 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (D₂O) δ = 146.5, 144.2, 141.8, 139.8, 127.4, 63.3, 60.4, 17.8.

[C₂OHmpip]Br: yield: 78% ¹H NMR (D₂O) δ = 3.94 (br, 2H), 3.41 (t, J (H, H) = 4.8 Hz, 2H), 3.24-3.38 (m, 4H), 3.02 (s, 3H), 1.78 (br, 4H), 1.52-1.59 (m, 2H). ¹³C NMR (D₂O) δ = 64.3, 62.3, 55.2, 49.0, 20.6, 19.7.

Synthesis of ILs 3-(2-hydroxyethyl)-1-methyl imidazolium tetrafluoroborate [C₂OHmim][BF₄], 1-(2-hydroxyethyl)-3-methyl pyridinium tetrafluoroborate [C₂OHmpy][BF₄], 1-(2-hydroxyethyl)-1-methyl piperidinium tetrafluoroborate [C₂OHmpip][BF₄], 3-(2-hydroxyethyl)-1-methyl imidazolium hexafluorophosphate [C₂OHmim][PF₆] and 3-(2-hydroxyethyl)-1-methyl

imidazolium bis(trifluoromethylsulfonyl)amide [C₂OHmim][Tf₂N] (Figure S1)

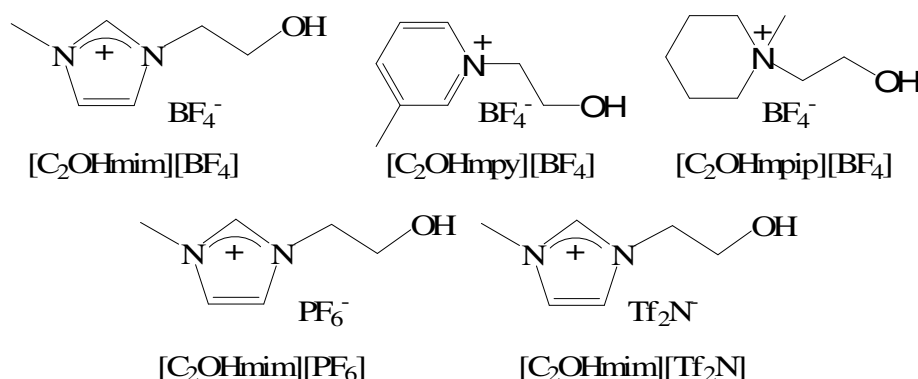


Figure S1: 5 Hydroxyl group functionalized ionic liquids synthesized.

[C₂OHmim][BF₄], [C₂OHmim][PF₆] have been reported before and the ILs described here were synthesized using the modified literature method.²

[C₂OHmim]Br (0.1 mol, 20.7 g) was dissolved in dry acetone and sodium tetrafluoroborate (0.1 mol, 11.0 g) (sodium hexafluorophosphate 0.1 mol, 16.8 g for [C₂OHmim][PF₆]) was added. The mixture was stirred for 3 days at 60°C. After filtration, the solvent was removed under vacuum. The product was further purified on a short alumina column (for [C₂OHmim][BF₄], [C₂OHmpy][BF₄], [C₂OHmpip][BF₄] using acetonitrile as eluent, for [C₂OHmim][PF₆] using MeOH:CH₂Cl₂, 1:2 as eluent). [C₂OHmpy][BF₄], [C₂OHmpip][BF₄] and [C₂OHmim][PF₆] were synthesized similarly.

[C₂OHmim][BF₄]: yield 52%, ¹H NMR (D₂O) δ = 8.73 (s, 1H), 7.57 (s, 1H), 7.51 (s, 1H), 4.38 (t, J (H, H) = 4.8 Hz, 2H), 3.92-4.00 (m, 5H). ¹³C NMR (D₂O) δ = 136.5, 123.8, 122.6, 60.2, 51.7, 35.8. ¹⁹F NMR (D₂O) δ = -150.6 (s).

[C₂OHmpy][BF₄]: yield 63%, ¹H NMR (CD₃CN) δ = 8.62 (s, 1H), 8.58 (d, J (H, H) = 8.0 Hz, 1H), 8.47 (d, J (H, H) = 8.0 Hz, 1H), 7.94 (t, J (H, H) = 8.0 Hz, 1H), 4.57 (t, J (H, H) = 4.8 Hz, 2H), 3.96 (t, J (H, H) = 4.8 Hz, 2H), 3.39 (s, 1H), 2.55 (s, 3H). ¹⁹F NMR (D₂O) δ = -152.0 (s).

[C₂OHmpip][BF₄]: yield 65%, ¹H NMR (D₂O) δ = 3.97 (br, 2H), 3.49 (t, J (H, H) = 4.8 Hz, 2H), 3.28-3.42 (m, 4H), 3.01 (s, 3H), 1.82 (br, 4H), 1.56-1.65 (m, 2H). ¹⁹F NMR (D₂O) δ = -151.2 (s).

[C₂OHmim][PF₆]: yield 72%, ¹H NMR (CD₃CN) δ = 8.59 (s, 1H), 7.43 (s, 1H), 7.36 (s, 1H), 4.24 (t, J (H, H) = 4.8 Hz, 2H), 3.86 (s, 3H), 3.82 (t, J (H, H) = 4.8 Hz, 2H). ¹⁹F NMR (CD₃CN) δ = -73.3 (d, J (F-P) = 717.2 Hz). ³¹P NMR (CD₃CN) δ = -144.6 (septet, J (P-F) = 717.2 Hz).

Synthesis of [C₂OHmim][Tf₂N]

Li(N[SO₂CF₃]₂) (0.05 mol, 14.4 g) was added to a solution of [C₂OHmim]Br (0.05 mol, 10.2 g) in water (10 ml) at room temperature. The IL phase was separated and washed with water (3 \times 5 ml) and dried under vacuum overnight. Yield 70 %, ¹H NMR (CD₃CN) δ = 8.50 (s, 1H), 7.43 (s, 1H), 7.37 (s, 1H), 4.23 (t, J (H, H) = 4.8 Hz, 2H), 3.87 (s, 3H) 3.83 (t, J (H, H) = 4.8 Hz, 2H). ¹³C NMR (CD₃CN) δ = 136.3, 123.4, 122.8, 120.0 (q, J (C-F) = 318.6 Hz) 60.2, 51.7, 35.8. ¹⁹F NMR (CD₃CN) δ = -80.6 (s).

Solubility test of PVP in [C₂OHmim][BF₄] and [C₂mim][BF₄]

5 g [C₂OHmim][BF₄] and [C₂mim][BF₄] were located in two 10 ml flasks and dried under vacuum at 60 °C prior to use. A known amount (for [C₂mim][BF₄], 25 mg was used and for [C₂OHmim][BF₄], 50 mg was used) of PVP (MW: 58000) was then added to each ionic liquid with stirring at 60 °C. After 1 h, [C₂mim][BF₄] solution still looked cloudy with white PVP powder sticking on the surface of the flask while [C₂OHmim][BF₄] forms a clear and homogenous solution. Another 50 mg PVP was then added into [C₂OHmim][BF₄] and it became clear again within 30 min. After 5 times adding, the solution remains clear and homogenous. The solution was cooled to r.t. and no change of the solution can be observed. Thus, the solubility of PVP in [C₂OHmim][BF₄] is at least 5% (Figure S3).

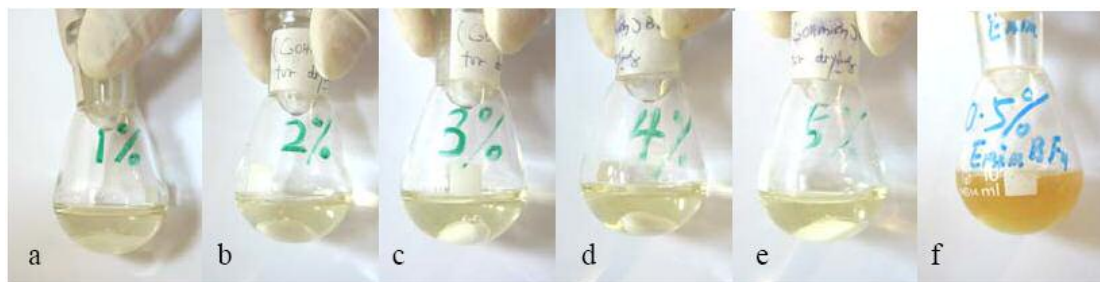


Figure S3: PVP solution in $[C_2OHmim][BF_4]$ (a-e) and $[C_2mim][BF_4]$ (f).

Preparation of Rh nanoparticles

$RhCl_3 \cdot xH_2O$ (0.5 mmol, 120 mg) was dissolved in a mixture of ethanol (80 ml) and water (20 ml) and PVP was added (550 mg, for recycling experiment 1.1 g was used, average MW: 58000). The mixture was refluxed for 2 h during which time the color of the solution changes from orange to black. The resulting Rh nanoparticle solution was kept at ambient temperature for further use.

Preparation of PVP-Rh- $[C_2OHmim][BF_4]$ system

A stock solution rhodium nanoparticles (10 ml) was added to $[C_2OHmim][BF_4]$ (20 ml). The ethanol and water were removed under reduced pressure on a rotary evaporator, followed by azeotropic evaporation with dried ethanol three times (3×40 ml). Other PVP-Rh-functionalized IL systems were prepared in a similar manner (pictures are shown in Figure S2).

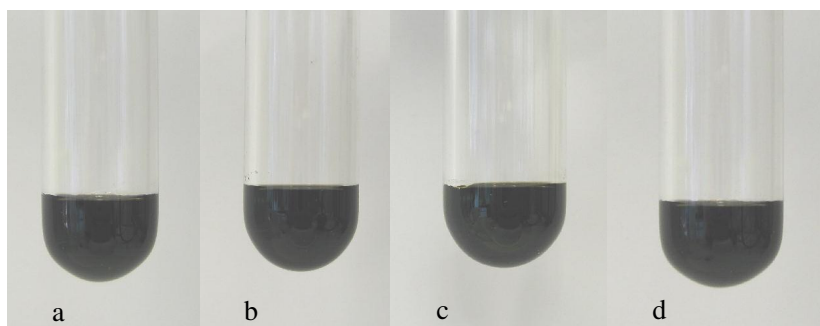


Figure S3: Rh nanoparticles immobilized in (a) $[C_2OHmim][PF_6]$, (b) $[C_2OHmim][Tf_2N]$, (c) $[C_2OHmpy][BF_4]$ and (d) $[C_2OHmpip][BF_4]$.

Catalytic hydrogenation procedures

All hydrogenation reactions were conducted in a home-built multicell autoclave containing an internal temperature probe. Glass reactor vessels were charged with 5 mmol (S to C = 2000) or 10 mmol (S to C = 4000), IL (1 ml) containing 2.5×10^{-3} M rhodium nanoparticles and octane (0.1 ml) as internal standard. The autoclave was purged with H_2 (3×10 bar), pressurized with H_2 (50 bar) and then heated to 40 °C. After 2 h, reactions were stopped and autoclave was cooled to ambient temperature using an external water-cooling system and the pressure was then released. Conversions were determined by GC analysis of the upper organic phase. Recycling experiments were carried out as follows: after reaction, the upper layer (mainly ethyl benzene) and IL phase were separated by decantation. Then, hexane (3 x 2 ml) was used to extract the IL phase thoroughly. Finally, the IL phase was maintained under vacuum for 12 h.

Table S1: Recycling experiments for the hydrogenation of styrene in $[C_2OHmim][BF_4]$ and $[C_2mim][BF_4]$.

Entry	ILs	Yields (%)	
		ethylbenzene	ethylcyclohexane
1	$[C_2OHmim][BF_4]$ (batch 1)	99.8	0.2
2	$[C_2OHmim][BF_4]$ (batch 2)	99.8	0.2
3	$[C_2OHmim][BF_4]$ batch 3)	99.7	0.3
4	$[C_2OHmim][BF_4]$ batch 4)	99.6	0.4
5	$[C_2OHmim][BF_4]$ (batch 5)	99.4	0.6
6	$[C_2OHmim][BF_4]$ (batch 6)	99.2	0.8
7	$[C_2OHmim][BF_4]$ (batch 7)	99.4	0.6
8	$[C_2OHmim][BF_4]$ (batch 8)	94.4	0.1
9	$[C_2OHmim][BF_4]$ (batch 9)	89.5	0.1
10	$[C_2mim][BF_4]$ (batch 1)	21.5	0
11	$[C_2mim][BF_4]$ (batch 2)	20.0	0
12	$[C_2mim][BF_4]$ (batch 3)	14.8	0

13	[C ₂ mim][BF ₄] (batch 4)	21.1	0
14	[C ₂ mim][BF ₄] (batch 5)	11.5	0

a Conditions: 2.5×10^{-3} mmol of Rh nanoparticles (Rh:PVP = 1:20) in [C₂OHmim][BF₄] (1 ml) or [C₂mim][BF₄] (1 ml), cat:sub = 4000:1, H₂ (50 bar) and at 40 ° C for 2 h.. Conversion determined by GC.

H₂ solubility in [C₂OHmim][BF₄]

[C₂OHmim][BF₄] (2.5 ml) was sealed in a sapphire NMR tube at a pressure of 100 atm H₂. After vigorous shaking for 4 h, a ¹H NMR spectrum of the solution was recorded on a 360 MHz Bruker NMR instrument. The ¹H NMR spectrum was fitted with WINNMR and NMRICMA2.8/MATALAB programs (nonlinear least squares fit, minimizing the difference between the measured and calculated spectra to determine the spectral parameters and integrals). The Henry's constant for H₂ was found to be 1.43×10^{-3} /MPa and the hydrogen concentration 0.47 mM at 1 atm (for [C₄mim][BF₄], the value is 0.86 mM).³

Determination of leaching of PVP-Rh-[C₂OHmim][BF₄] and PVP-Rh-[C₂mim][BF₄] into organic solvents

PVP-Rh-[C₂OHmim][BF₄] or PVP-Rh-[C₂mim][BF₄] (1 ml) was dried at 70 °C under vacuum for 12 h. After cooled to 25 °C, 1 ml of organic solvent (hexane, diethyl ether, ethyl acetate, dichloromethane and chloroform) were added into the IL and stirred vigorously for 2 h and then kept still for another 2 h. A known amount of organic phase (0.4-0.6 ml) was then removed, dried under vacuum and the residue was dissolved in CD₃CN containing styrene (10 µL) as internal standard. The amount of IL was obtained by a comparison of the NMR integration of 2-H from imidazolium ring (8.49 ppm for [C₂OHmim][BF₄] and 8.40 ppm for [C₂mim][BF₄]) and one of the protons from the double bond in styrene (5.2 ppm).

Table S2: Solubility of [C₂mim][BF₄] and [C₂OHmim][BF₄] in organic solvents (10³ M) at 25 °C.

ILs \ Ext.	CH ₂ Cl ₂	CHCl ₃	Ethyl acetate	Diethyl ether	n-C ₆ H ₁₄
[C ₂ mim][BF ₄]	Miscible	Miscible	6.0	0.16	- ^a
[C ₂ OHmim][BF ₄]	9.1	3.9	2.3	- ^a	- ^a

a. Not detected.

Catalyst leaching

After reaction, the upper layer (containing the product and unreacted substrate) as well as the hexane extracts (ca. 8 ml) were combined and the volatile components were removed under reduced pressure. The residue was digested by refluxing in a mixture of H₂O₂/HClO₄ for 4 h and then by refluxing in aqua regia for another 4 h. The solution was evaporated to ca. 1 ml, diluted with 2 % HNO₃ to 10 ml which was delivered to ICP analysis.

TEM Sample Preparation

The Rh nanoparticle solution (0.05 ml) was diluted with deionized water (0.2 ml) and sonicated for 10 min. One drop of the solution was then deposited onto a carbon coated copper grid (500 mesh) and dried under vacuum for 12 h. The size distribution is based estimates from 100-200 particles.

Characterization of polystyrene in PVP-Rh-[C₂OHmim][BF₄] after recycling

After nine batches the white material in PVP-Rh-[C₂OHmim][BF₄] (0.1 ml) was extracted using ethyl acetate (1 ml). The ethyl acetate phase was concentrated to about 0.1 ml and was transferred to a KBr window. After all organic solvent has evaporated and IR spectrum was recorded. The IR spectrum (Figure S3), shows peaks that belong to the IL (NMR leaching experiments also show ILs will be leached by ethyl acetate). By comparison to authentic samples, the characteristic peaks for polystyrene (PS) are present in the final extract, giving unambiguous evidence for the presence of PS after

reaction.

Peaks corresponding to PS (cm^{-1}):

Sample from the reaction: 3082, 3059, 3025, 2924, 2853, 1945, 1872, 1802, 1601, 1492, 1452, 746, 697.

Authentic PS: 3082, 3059, 3025, 2922, 2850, 1946, 1870, 1804, 1601, 1492, 1452, 747, 697.

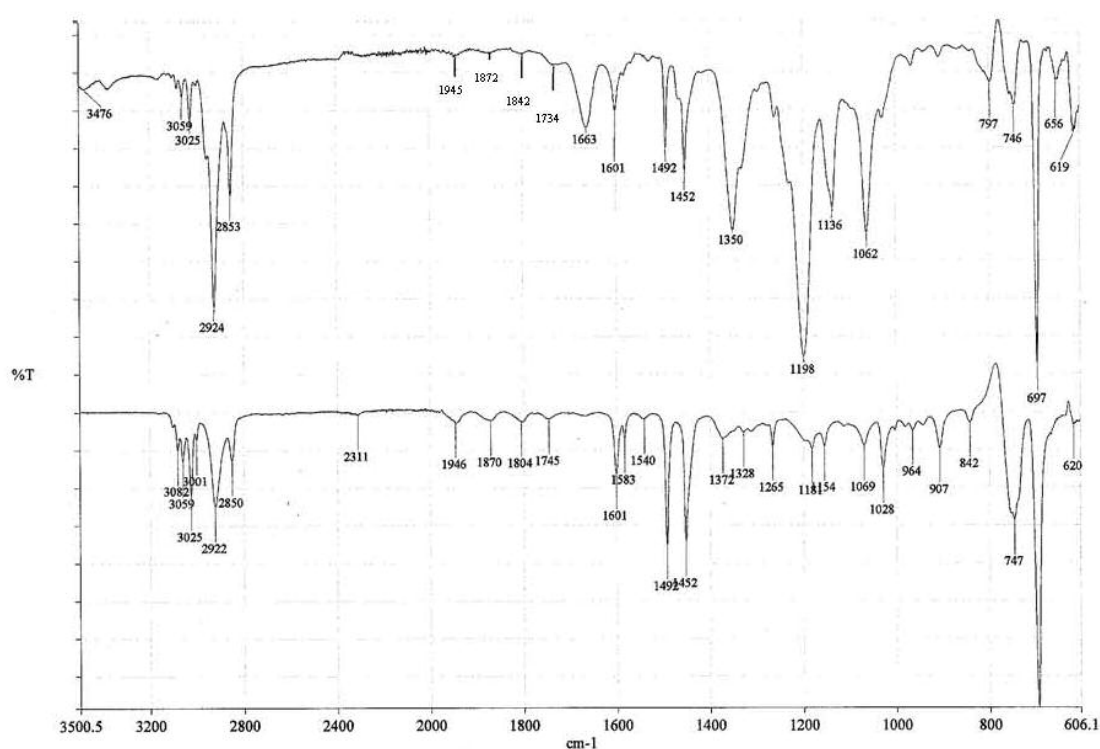


Figure S4: IR spectrum of top. extractants of final PVP-Rh-[C₂OHmim][BF₄], below. authentic polystyrene (average MW: 280000).

References

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