Selective continuous flow removal of nitrogen impurities from oil containing S- and N-heteroaromatic compounds using metal-containing ionic liquids supported on monolithic silica with hierarchical porosity

Paulo Forte, Alexander Sachse, Michael Maes, Anne Galarneau and Dirk De Vos*

* Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, B-3001 Leuven (Belgium). Fax: (+32) 16 321998; Tel: (32) 16 321639; E-mail: dirk.devos@biw.kuleuven.be

Institut Charles Gerhardt Montpellier, UMR 5253, CNRS-UM2-ENSCM-UM1, ENSCM, 8 rue de l’École Normale, 34296 Montpellier Cedex 5 (France).

Electronic Supplementary information

Synthesis of the bistriflimide metal salts.

Synthesis of copper(II) bis(trifluoromethanesulfonyl)imide pentahydrate salt \(\text{Cu}^{II}(\text{NTf}_2)_2\cdot5\text{H}_2\text{O}\).

Copper(II) oxide (CuO) was gradually added to an aqueous solution of bis(trifluoromethanesulfonyl)imidic acid. When no more copper salt was consumed, the remaining solid was filtered out and the water evaporated in a Schlenk setup under <10⁻³ mbar to afford the copper(II) bistriflimide salt \(\text{Cu}(\text{NTf}_2)_2\cdot5\text{H}_2\text{O}\) in blue crystals. Literature procedure (Nie J. et al., Catalysis Today, 1997 36(1) p. 81-84).

Synthesis of copper(I) bis(trifluoromethanesulfonyl)imide salt \(\text{Cu}^I(\text{NTf}_2)_2\) in IL \([\text{BMIM}][\text{NTf}_2]\]

\(\text{Cu}^I(\text{NTf}_2)_2\cdot5\text{H}_2\text{O}\) (140 mg, 0.196 mmol) was transferred under \(\text{N}_2\) atmosphere to a round-bottomed flask. Dry \([\text{BMIM}][\text{NTf}_2]\) (10 ml) was added and salt was dissolved at 90 °C and under vacuum. The solution presented a pale green colour. Metallic copper (12.46 mg, 0.196 mmol) was added and the mixture was stirred at 90 °C overnight under vacuum. After this period, the copper source in contact with the solution presented signs of corrosion and the solution presented a light-brown colour. The mass measurement of the copper source before and after the reaction confirms a 90% symproportionation reaction completion.

Synthesis of zinc(II) bis(trifluoromethanesulfonyl)imide \(\text{Zn}^{II}(\text{NTf}_2)_2\).

Zinc(II) oxide was added to a solution of bis(trifluoromethanesulfonyl)imidic acid in deionized water. When no more oxide was consumed, the remaining solid was filtrated out. The water was evaporated in a schlenk setup under <10⁻³ mbar and the resulting off-white powder was dried under vacuum at 100 °C. Literature procedure (Nie J., et al., Catalysis Today, 1997 36(1) p. 81-84).

Synthesis of iron(II) bis(trifluoromethanesulfonyl)imide \(\text{Fe}^{II}(\text{NTf}_2)_2\).

Metallic iron (1 g, 17.91 mmol) was suspended in water (Volume: 5 ml) under \(\text{N}_2\) atmosphere. The bis(trifluoromethanesulfonyl)imidic acid (12.59 g, 35.8 mmol) was added, dropwise. The colourless, clear solution was stirred for a few minutes at 80 °C. The solvent was removed under 10⁻³ mbar
Synthesis of the [MCl₄]-type ionic liquids:

**Synthesis of 1-Butyl-3-methylimidazolium copper(I) dichloride [BMIM][CuICl₂] ionic liquid.**

[BMIM][Cl] (4 g, 22.90 mmol) and copper(I) chloride (2.27 g, 22.93 mmol) were mixed, under N₂ atmosphere. The solid-state mixture was stirred under vacuum at room temperature until complete dissolution of the components. After all the residual water was evaporated, the liquid obtained presented a brown colour. Literature reaction (Bolkan, S.A. and J.T. Yoke, *J Chem Eng Data*, 1986 31(2): p. 194-197).

**Synthesis of bis(1-Butyl-3-methylimidazolium) copper(II) tetrachloride [BMIM]₂[CuIICl₄] ionic liquid.**

Copper(II) chloride (1.328 g, 9.88 mmol) and [BMIM][Cl] (3.45 g, 19.75 mmol) were mixed, under N₂ atmosphere. The solid-state mixture was stirred under vacuum at 80 ºC until complete dissolution of the components. After all the residual water was evaporated, the liquid obtained presented a brownish-red colour. Literature reaction (Sasaki, T., et al., *Chem Commun*, 2005 (19) p. 2506-2508).

**Synthesis of bis(1-Butyl-3-methylimidazolium) zinc(II) tetrachloride [BMIM]₂[ZnIICl₄] ionic liquid.**

Zinc chloride (3.12 g, 22.90 mmol) and [BMIM][Cl] (4 g, 22.90 mmol) were mixed, under N₂ atmosphere. The solid-state mixture was stirred under vacuum at room temperature until complete dissolution of the components. After all the residual water was evaporated, the liquid obtained presented a light yellow colour. Literature reaction (Seddon, K.R., et al., *Inorg Chem*, 2011 50(11) p. 5258-5271).

**Synthesis of 1-Butyl-3-methylimidazolium iron(II) tetrachloride [BMIM]₂[FeIICl₄] ionic liquid.**

[BMIM][Cl] (0.993 g, 5.68 mmol) and iron(II) chloride tetrahydrate (1.130 g, 5.68 mmol) were mixed, under N₂ atmosphere. The solid-state mixture was stirred under vacuum at room temperature until complete dissolution of the components. After all the residual water was evaporated, the liquid obtained presented a brown colour. Literature reaction (Sitze, M.S., et al., *Inorganic Chemistry*, 2001 40(10) p. 2298-2304.)

**Synthesis of 1-Butyl-3-methylimidazolium iron(III) tetrachloride [BMIM][FeIIICl₄] ionic liquid.**

[BMIM][Cl] (0.993 g, 5.68 mmol) and iron(III) trichloride (0.924 g, 5.70 mmol) were mixed, under N₂ atmosphere. The solid-state mixture was stirred under vacuum at room temperature until complete dissolution of the components. After all the residual water was evaporated, the liquid obtained presented a brown colour. Literature reaction (Sitze, M.S., et al., *Inorganic Chemistry*, 2001 40(10) p. 2298-2304.)