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

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Electronic Supplementary information

Synthesis of the bistriflimide metal salts.

Synthesis of copper(II) bis(trifluoromethanesulfonyl)imide pentahydrate salt {$Cu^{II}(NTf_2)_2.5H_2O$}.
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 $Cu(NTf_2)_2.5H_2O$ 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 (Cu^INtf_2) in IL [BMIM][NTf_2]
$Cu(II)(NTf_2)_2.5H_20$ (140 mg, 0.196 mmol) was transferred under N_2 atmosphere to a round-bottomed flask. Dry [BMIM][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 {$Zn^{II}(NTf_2)_2$}.
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 ºC. Literature procedure (Nie J., *et al.*, *Catalysis Today*, 1997 **36**(1) p. 81-84).

Synthesis of iron(II) bis(trifluoromethanesulfonyl)imide salt {$Fe^{II}(NTf_2)_2$}.
Metallic iron (1 g, 17.91 mmol) was suspended in water (Volume: 5 ml) under 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

reduced pressure in a Shlenk setup pressure, resulting in a white powder. Literature procedure (Yamagata, M., et al., *Electrochimica Acta*, 2007. **52**(9): p. 3317-3322).

Synthesis of the [MCl_x]-type ionic liquids:

Synthesis of 1-Butyl-3-methylimidazolium copper(I) dichloride [BMIM][$Cu^{I}Cl_2$] ionic liquid.

[BMIM][Cl] (4 g, 22.90 mmol) and copper(I) chloride (2.27 g, 22.93 mmol) were mixed, under N_2 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]$_2$[$Cu^{II}Cl_4$] ionic liquid.

Copper(II) chloride (1.328 g, 9.88 mmol) and [BMIM][Cl] (3.45 g, 19.75 mmol) were mixed, under N_2 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]$_2$[$Zn^{II}Cl_4$] ionic liquid.

Zinc chloride (3.12 g, 22.90 mmol) and [BMIM][Cl] (4 g, 22.90 mmol) were mixed, under N_2 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]$_2$[$Fe^{II}Cl_4$] ionic liquid.

[BMIM][Cl] (0.993 g, 5.68 mmol) and iron(II) chloride tetrahydrate (1.130 g, 5.68 mmol) were mixed, under N_2 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][$Fe^{III}Cl_4$] ionic liquid.

[BMIM][Cl] (0.993 g, 5.68 mmol) and iron(III) trichloride (0.924 g, 5.70 mmol) were mixed, under N_2 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.)