Supporting Information

An efficient Pt nanoparticle-ionic liquid system for the hydrodeoxygenation of bio-derived phenols under mild conditions

Lu Chen,ª Cornel Fink,ª Zhaofu Fei,ª Paul J. Dysonª,* and Gabor Laurenczyª,*
1. Characterization of ILs

1) [Emim]NTf₂

Figure S1 The ¹H NMR spectrum of [Emim]NTf₂ dissolved in d6-DMSO at ambient conditions
[Emim]NTf₂: ¹H-NMR (DMSO, 400MHz): δ (ppm) = 9.10 (s, 1H, NCHN), 7.76–7.77 (t, 1H, CH₃NCHCH[N]), 7.68 (t, 1H, CH₃NCHCHN), 4.17–4.21 (m, 2H, NCH₂CH₃), 3.85 (s, 3H, NCH₃), 1.41–1.43 (t, 3H, NCH₂CH₃).

2) [Bmim]PF₆

Figure S2 The ¹H NMR spectrum of [Bmim]PF₆ dissolved in d6-DMSO at ambient conditions
[Bmim]PF₆: ¹H-NMR (DMSO, 400MHz): δ (ppm) = 9.08 (s, 1H, NCHN), 7.74–7.75 (t, 1H, CH₃NCHCHN), 7.68 (t, 1H, CH₃NCHCHN), 4.15–4.17 (t, 2H, NCH₂(CH₂)₂CH₃), 3.85 (s, 3H, NCH₃), 1.77 (m, 2H, NCH₂CH₂CH₂CH₃), 1.27 (m, 2H, N(CH₂)₂CH₂CH₃), 0.89–0.92 (t, 3H, N(CH₂)₃CH₃).
3) [Bmim]BF$_4$

Figure S3 The $^1$H NMR spectrum of [Bmim]BF$_4$ dissolved in d6-DMSO at ambient conditions

[Bmim]BF$_4$: $^1$H-NMR (DMSO, 400MHz): $\delta$ (ppm) = 9.07 (s, 1H, NCHN), 7.74–7.75 (t, 1H, CH$_3$NCHCHN), 7.68 (t, 1H, CH$_3$NCHCHN), 4.15–4.17 (t, 2H, NCH$_2$(CH$_2$)$_2$CH$_3$), 3.85 (s, 3H, NCH$_3$), 1.77 (m, 2H, NCH$_2$CH$_2$CH$_3$), 1.27 (m, 2H, N(CH$_2$)$_2$CH$_3$), 0.89–0.92 (t, 3H, N(CH$_2$)$_3$CH$_3$).

Catalytic reactions

Table S1 Yields of products and conversion of phenol over Pt NPs prepared in different ILs

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<th>Con (%)</th>
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ILs2: [Bmim]PF$_6$; LA: Lewis acid; BA: Brønsted acid; Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; DOR: deoxygenation rate; Di-E: dicyclohexyl ether; Bi-ane: cyclohexylcyclohexane (bicyclohexane)

a: without Pt; b: without [Emim]NTf$_2$; c: 130 °C

Reaction conditions: [Emim]NTf$_2$ (2.0 g), ILs2/LA/BA (0.5 g/0.2 g/0.2 g), H$_2$PtCl$_6$ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H$_2$, 60 °C, 15 h. Reproducibility of results is ±5 %.


Table S2 Yields of products and conversion of phenol over different NPs precursors in ILs

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Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; DOR: deoxygenation rate; Di-E: dicyclohexyl ether; Bi-ane: cyclohexylcyclohexane (bicyclohexane); Cy-one: cyclohexylcyclohexanone

a: without [Bmim]PF$_6$; b: without [Emim]NTf$_2$

Reaction conditions: [Emim]NTf$_2$ (2.0 g), [Bmim]PF$_6$ (0.5 g), H$_2$PtCl$_6$ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H$_2$, 60 °C, 15 h. Reproducibility of results is ±5 %.
Recycling Experiments

Table S3 Catalyst recycling of Pt NPs/ILs for phenol

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Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; DOR: deoxygenation rate; Di-E: dicyclohexyl ether; Bi-ane: cyclohexylcyclohexane (bicyclohexane); Cy-one: cyclohexylcyclohexanone

Reaction conditions: [Emim]NTf$_2$ (2.0 g), [Bmim]PF$_6$ (0.5 g), H$_2$PtCl$_6$ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H$_2$, 60 °C, 15 h. Reproducibility of results is ±5 %.

As the Table S3 shows, after recycling once, the selectivity of cyclohexane is still high, while the conversion of phenol is decreasing. The inactivation of the catalyst may be caused by the increase of the size of the NPs after each reaction. The loss of NPs in each run may be another main reason.

Fig. S4 TEM micrograph and histogram showing the size distribution of Pt NPs after three times recycling in [Emim]NTf$_2$-[Bmim]PF$_6$

D$_{\text{mean}}$ = 4.4 nm
Fig. S5 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmmim]PF$_6$

D$_{\text{mean}} = 3.6$ nm

Fig. S6 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmpy]PF$_6$

D$_{\text{mean}} = 3.7$ nm
Fig. S7 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmim]OTf

$D_{\text{mean}} = 3.5$ nm

Fig. S8 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmim]BF$_4$

$D_{\text{mean}} = 3.9$ nm
Effects of metal precursors

In extension to the above work, further different metal NPs were tested for HDO of phenol to cyclohexane (Table S4). Based on our measurements, platinum is the best for HDO of phenol in terms of activity and yield, followed by rhodium, palladium, and ruthenium. The Pt NPs were more active than other metals, and provided the highest yield of cyclohexane. The reason for the inhibited activity of ruthenium is that RuCl$_3$ is not completely reduced at the given reaction conditions. In mechanistic terms, the decreased performance of Pd and Rh is directly linked to their ability to hydrogenate the aromatic ring of phenol.

The platinum salt precursors play a vital role in the reactions. Since the solubility of H$_2$PtCl$_6$ is the highest in ILs, the performance of H$_2$PtCl$_6$ in HDO is better than K$_2$PtCl$_4$ or PtO$_2$. Our newly developed NPs/ILs systems has a notable better performance for hydrogenating phenol than the well-studied heterogeneous catalyst Pt/C and Pt-Ni$_2$P/C. The Pt-Ni$_2$P/C was synthesised followed by the reported method.$^1$

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Fig. S9 TEM micrograph and histogram showing the size distribution of Pt NPs in [Bmim]PF$_6$

D$_{\text{mean}}$ = 5.5 nm
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Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; DOR: deoxygenation rate

Reaction conditions: [Emim]NTF₂ (2.0 g), [Bmim]PF₆ (0.5 g), H₂PtCl₆ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H₂, 60 °C, 15 h. Reproducibility of results is ±5 %.

Fig. S10 The full XPS pattern of the Pt NPs
Fig. S11 The ESI-MS figure of the mixture after the reaction