Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

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

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1. Characterization of ILs

1) [Emim]NTf_2

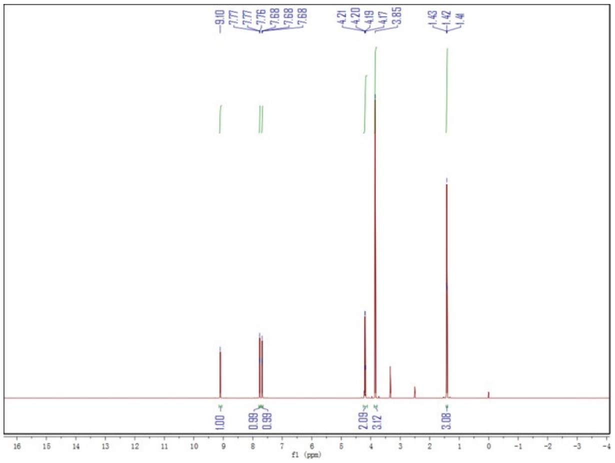

Figure S1 The ^1H NMR spectrum of [Emim]NTf_2 dissolved in d6-DMSO at ambient conditions

[Emim]NTf_2: ^1H-NMR (DMSO, 400MHz): δ (ppm) = 9.10 (s, 1H, $NC\underline{H}N$), 7.76−7.77 (t, 1H, $CH_3NCHC\underline{H}N$), 7.68 (t, 1H, $CH_3NC\underline{H}CHN$), 4.17−4.21 (m, 2H, $NC\underline{H}_2CH_3$), 3.85 (s, 3H, $NC\underline{H}_3$), 1.41−1.43 (t, 3H, $NCH_2C\underline{H}_3$).

2) [Bmim]PF_6

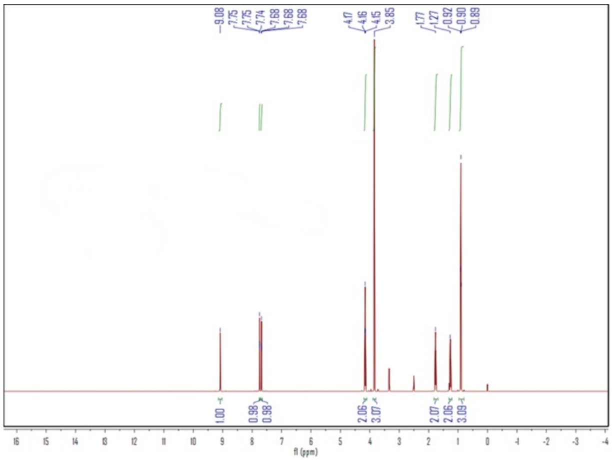

Figure S2 The ^1H NMR spectrum of [Bmim]PF_6 dissolved in d6-DMSO at ambient conditions

[Bmim]PF_6: ^1H-NMR (DMSO, 400MHz): δ (ppm) = 9.08 (s, 1H, $NC\underline{H}N$), 7.74−7.75 (t, 1H, $CH_3NCHC\underline{H}N$), 7.68 (t, 1H, $CH_3NC\underline{H}CHN$), 4.15−4.17 (t, 2H, $NC\underline{H}_2(CH_2)_2CH_3$), 3.85 (s, 3H, $NC\underline{H}_3$), 1.77 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 1.27 (m, 2H, $N(CH_2)_2C\underline{H}_2CH_3$), 0.89−0.92 (t, 3H, $N(CH_2)_3C\underline{H}_3$).

3) [Bmim]BF_4

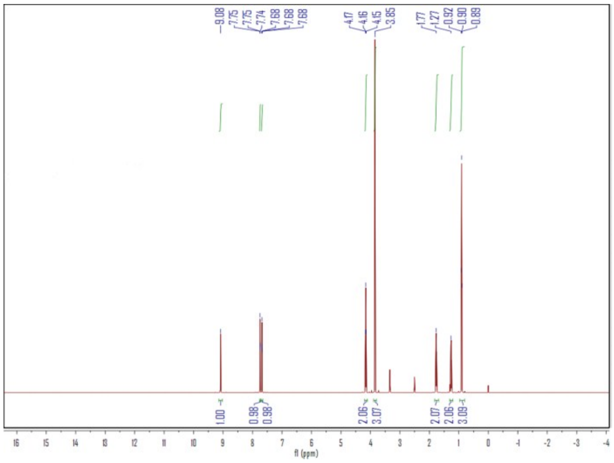

Figure S3 The ^{1}H NMR spectrum of [Bmim]BF_4 dissolved in d6-DMSO at ambient conditions

[Bmim]BF_4: ^{1}H-NMR (DMSO, 400MHz): δ (ppm) = 9.07 (s, 1H, $NC\underline{H}N$), 7.74−7.75 (t, 1H, $CH_3NCHC\underline{H}N$), 7.68 (t, 1H, $CH_3NC\underline{H}CHN$), 4.15−4.17 (t, 2H, $NC\underline{H_2}(CH_2)_2CH_3$), 3.85 (s, 3H, $NC\underline{H_3}$), 1.77 (m, 2H, $NCH_2C\underline{H_2}CH_2CH_3$), 1.27 (m, 2H, $N(CH_2)_2C\underline{H_2}CH_3$), 0.89−0.92 (t, 3H, $N(CH_2)_3C\underline{H_3}$).

Catalytic reactions

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

	ILs2/LA/BA	Con (%)	Sel (%)					
			-ane	-ene	-nol	-one	Di-E	Bi-ane
1[a]	[Bmim]PF_6	0	0	0	0	0	0	0
2	-	100	45	0	53	1	1	0
3	[Bmim]PF_6	100	86	8	0	0	5	1
4[b]	[Bmim]PF_6	100	84	8	0	0	7	1
5	[Bmim]OTf	49	54	0	27	19	0	0
6[b]	[Bmim]OTf	0	0	0	0	0	0	0
7[b,c]	[Bmim]OTf	52	59	0	10	31	1	0
8	[Bmim]BF_4	100	52	19	18	0	10	1
9[b]	[Bmim]BF_4	50	46	0	31	23	0	0
10	[Bmim]Cl	0	0	0	0	0	0	0
11[c]	[Bmim]Cl	45	45	0	21	34	0	0
12	[Emim]OAc	0	0	0	0	0	0	0
13	$[N(CH_3)_4]PF_6$	100	44	2	47	0	7	0
14	$[N(CH_3)_4]ClO_4$	100	50	0	41	6	3	0
15	[Bmmim]PF_6	100	61	13	17	3	6	0
16	[Bmpy]PF_6	75	63	5	18	5	8	1
17	$AlCl_3$	100	37	0	45	6	10	2
18	$ZnCl_2$	100	43	0	36	0	20	1
19	$Cu(OTf)_2$	10	71	12	0	0	16	1
20	H_3PO_4	100	56	0	42	0	2	0

21	HCl	55	45	0	39	15	1	0

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_2PtCl_6 (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H_2, 60 °C, 15 h. Reproducibility of results is ±5 %.

[Bmim]OTf: 1-Butyl-3-methylimidazolium trifluoromethanesulfonate; [Bmim]BF_4: 1-Butyl-3-methylimidazolium tetrafluoroborate; [Bmim]Cl: 1-Butyl-3-methylimidazolium chloride; [Emim]OAc: 1-Ethyl-3-methylimidazolium acetate; $[N(CH_3)_4]PF_6$: Tetraethylammonium hexafluorophosphate; $[N(CH_3)_4]ClO_4$: Tetramethylammonium perchlorate; [Bmmim]PF_6: 1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate; [Bmpy]PF_6: 1-butyl-4-methylpyridinium hexafluorophosphate.

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

	T (°C)	P (MPa)	t (h)	Con(%)	Sel (%)						
					-ane	-ene	-nol	-one	Di-E	Bi-ane	Cy-one
1[a]	60	0.1	15	100	47	0	29	24	0	0	0
2[a]	60	1	15	100	45	0	53	1	1	0	0
3[b]	40	1	15	100	67	18	9	1	4	0	1
4	60	0.1	15	100	60	6	19	0	10	0	5
5	60	1	15	100	86	8	0	0	5	1	0
6	60	2.5	15	100	87	7	0	0	6	0	0
7	60	5	15	100	86	7	0	0	5	2	0
8	25	1	15	69	42	1	53	5	0	0	0
9	40	1	15	100	58	18	19	0	4	1	0
10	60	1	15	100	86	8	0	0	6	0	0
11	80	1	15	100	88	4	0	0	7	1	0
12	40	1	15	100	58	18	19	0	5	0	0
13	40	2.5	15	100	59	19	21	0	1	0	0
14	60	1	5	100	47	8	22	14	6	1	2
15	60	1	10	100	71	11	10	0	6	0	2
16	60	1	20	100	85	11	0	0	1	3	0
17	60	1	25	100	84	13	0	0	1	2	0

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_2PtCl_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

	Con (%)	Sel (%)						
		-ane	-ene	-nol	-one	Di-E	Bi-ane	Cy-one
1	100	86	8	0	0	5	1	0
2	71	84	5	0	0	7	2	2
3	53	84	5	2	0	5	1	3

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_2PtCl_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.

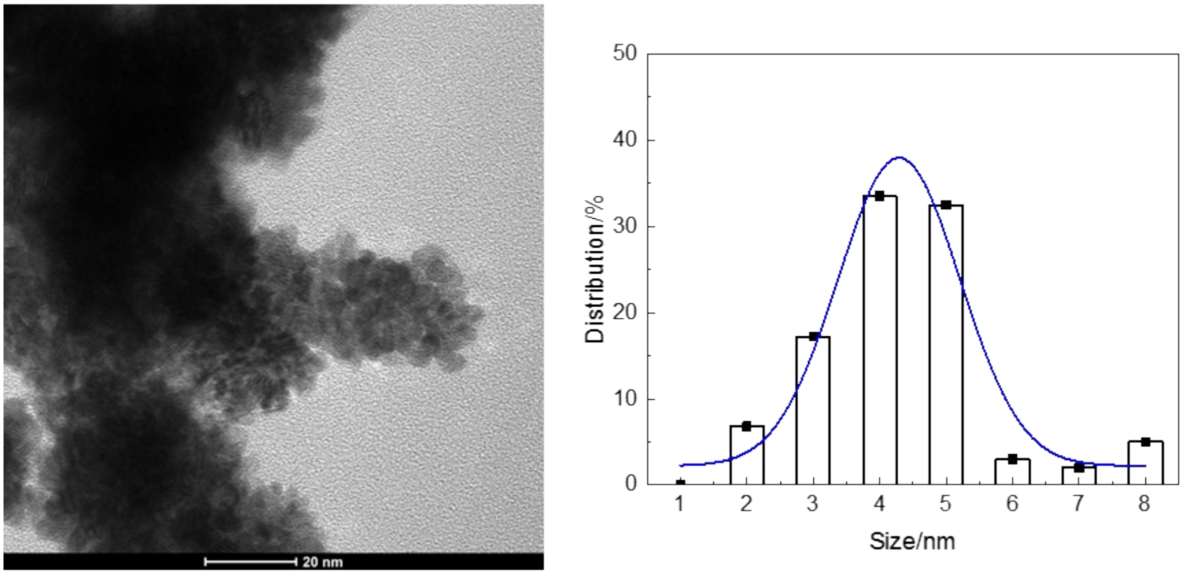

Fig. S4 TEM micrograph and histogram showing the size distribution of Pt NPs after three times recycling in [Emim]NTf$_2$-[Bmim]PF$_6$

D_{mean}= 4.4 nm

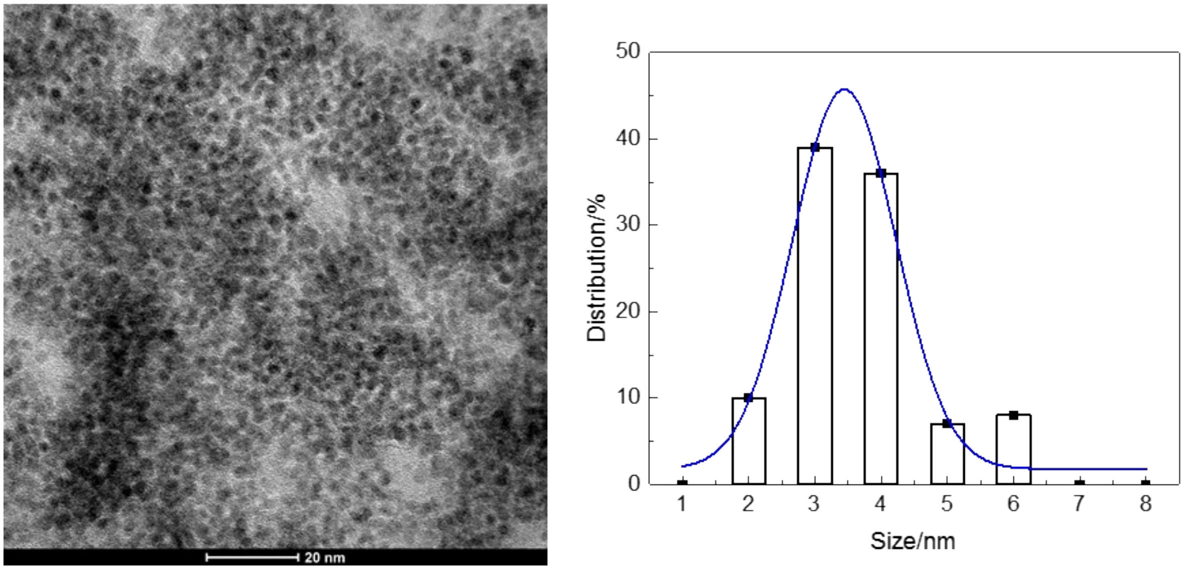

Fig. S5 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmmim]PF$_6$

D$_{mean}$= 3.6 nm

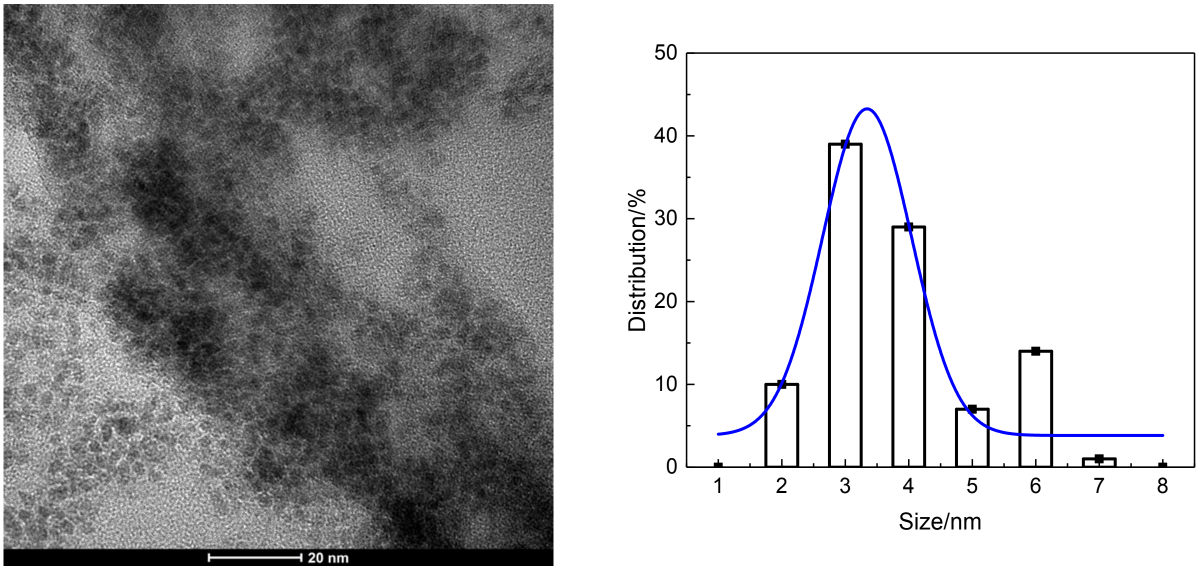

Fig. S6 TEM micrograph and histogram showing the size distribution of Pt NPs in [Emim]NTf$_2$-[Bmpy]PF$_6$

D$_{mean}$= 3.7 nm

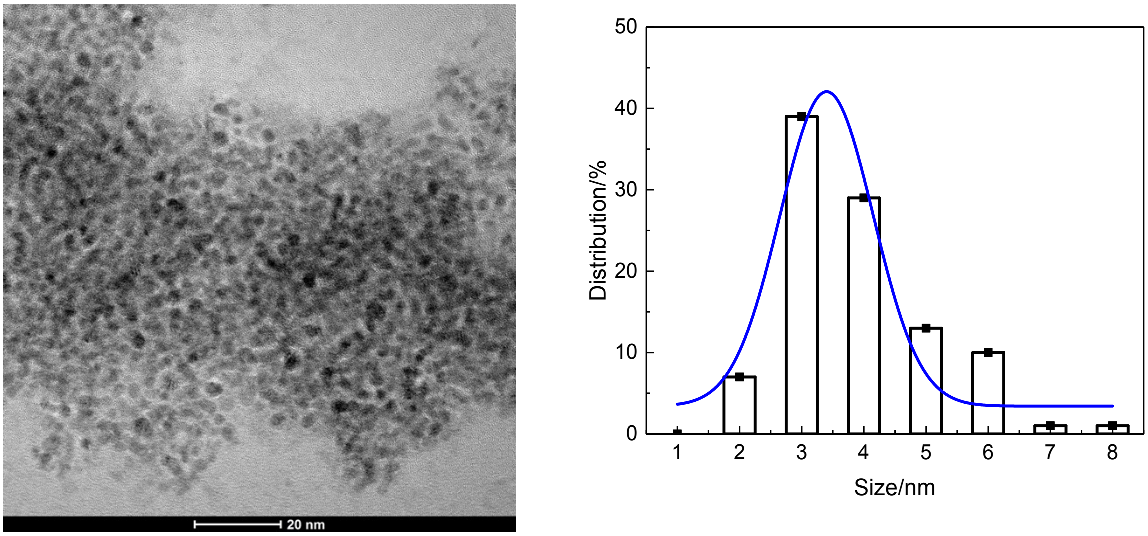

Fig. S7 TEM micrograph and histogram showing the size distribution of Pt NPs in $[Emim]NTf_2$-[Bmim]OTf

D_{mean}= 3.5 nm

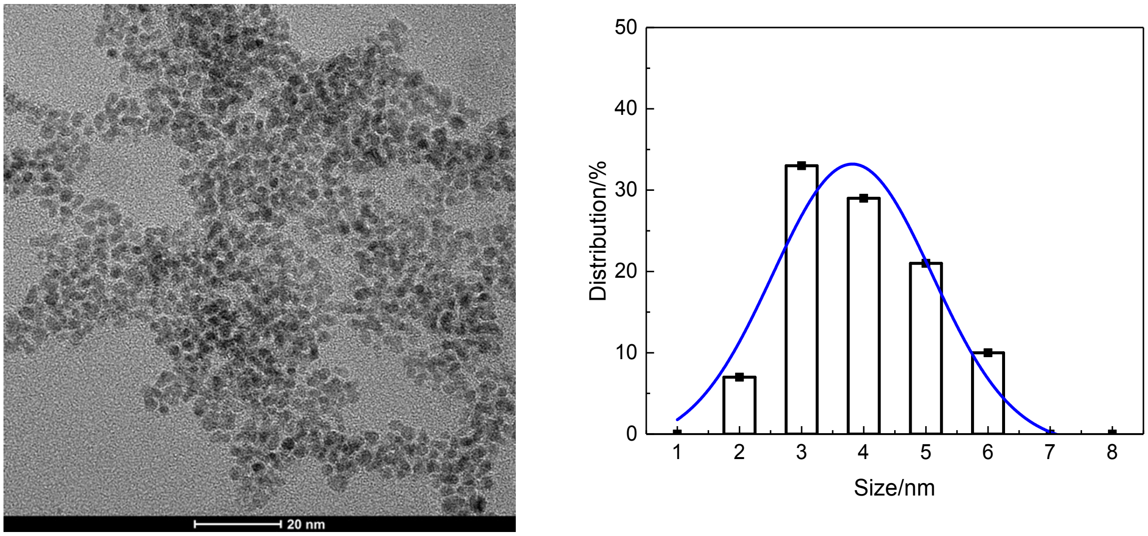

Fig. S8 TEM micrograph and histogram showing the size distribution of Pt NPs in $[Emim]NTf_2$-$[Bmim]BF_4$

D_{mean}= 3.9 nm

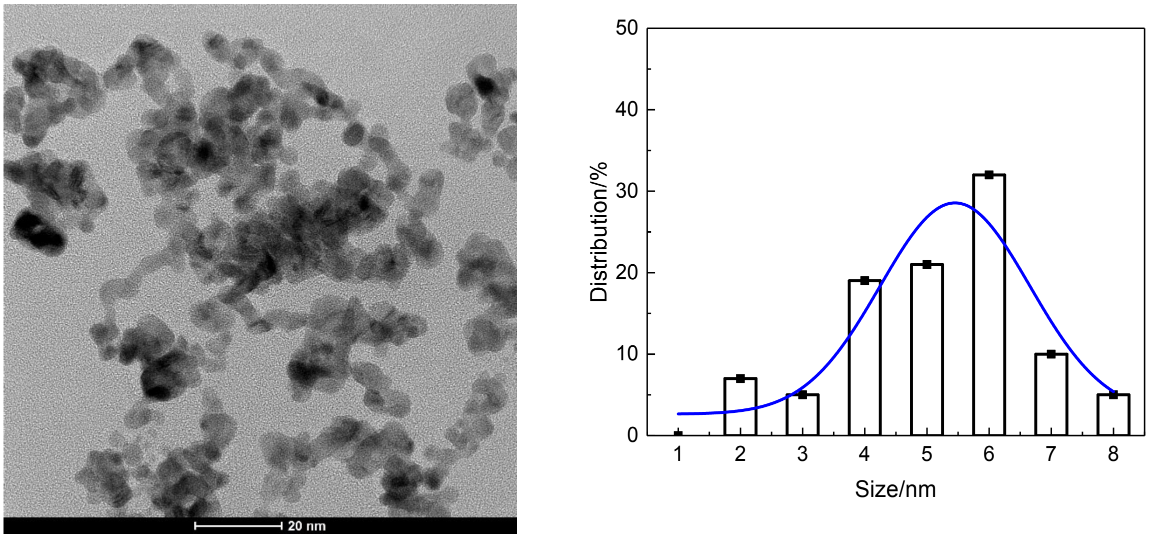

Fig. S9 TEM micrograph and histogram showing the size distribution of Pt NPs in [Bmim]PF_6

D_{mean}= 5.5 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_2PtCl_6 is the highest in ILs, the performance of H_2PtCl_6 in HDO is better than K_2PtCl_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_2P/C. The Pt-Ni_2P/C was synthesised followed by the reported method.[1]

Table S4 Yields of products and conversion of phenol over different NPs precursors in ILs

	NPs	Con (%)	Sel (%)				DOR
			-ane	-ene	-nol	-one	
1	H_2PtCl_6	100	86	8	0	0	94
2	K_2PtCl_4	100	63	18	13	0	81
3	PtO_2	99	25	0	71	4	25
4	Pt/C	0	0	0	0	0	0
5	Pt-Ni_2P/C	0	0	0	0	0	0
6	K_2PdCl_4	19	30	0	28	0	6
7	$RuCl_3$	0	0	0	0	0	0
8	$RhCl_3$	56	30	9	16	34	17

Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; DOR: deoxygenation rate

Reaction conditions: [Emim]NTF_2 (2.0 g), [Bmim]PF_6 (0.5 g), H_2PtCl_6 (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H_2, 60 °C, 15 h. Reproducibility of results is ±5 %.

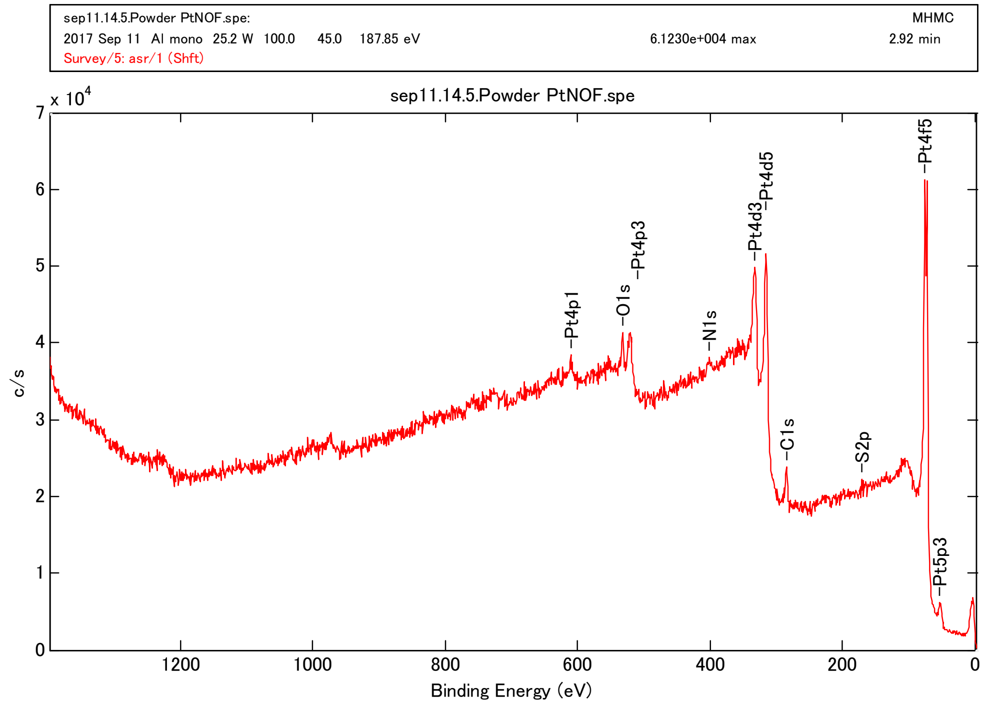

Fig. S10 The full XPS pattern of the Pt NPs

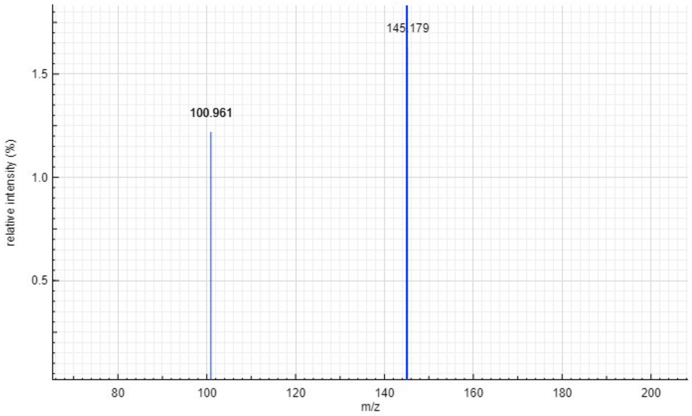

Fig. S11 The ESI-MS figure of the mixture after the reaction