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

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Platinum nanoparticles (NPs) were synthesized *in situ* in the ionic liquid (IL) [Emim]NTf₂ (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) as well as in mixtures of [Emim]NTf₂ with a second IL, Lewis acid or Brønsted acid, but in the absence of additional stabilizers. The resulting NP/IL systems catalyze the hydrodeoxygenation of phenol under mild conditions (60 °C, 1.0 MPa H₂), achieving full substrate conversion and high deoxygenation rate (over 95%) to cyclohexane and cyclohexene. The combination of [Emim]NTf₂ and [Bmim]PF₆ results in the best catalytic performance. Also the transformation of other substituted phenols and dimers such as catechol, guaiacol and diphenyl ether was studied in the Pt NP/[Emim]NTf₂-[Bmim]PF₆ system and in most cases afforded cyclohexane in good yield.

Introduction

Bio-oil derived from lignocellulose biomass is a promising renewable liquid fuel that could substitute petroleum, although it cannot be used directly to replace diesel due to its lower heating value and thermal instability.¹ The heating value of bio-oil is less than half that of conventional fuels, with an energy density of 19 MJ/kg.² Because of the high oxygen content of bio-oil, upgrading by hydrodeoxygenation (HDO) could be beneficial, increasing the energy density and thermal stability.

In HDO reactions, the solvent has a pronounced effect on both the conversion rate and on the selectivity.³ Therefore, an appropriate solvent is crucial for an efficient catalytic process. Many excellent aqueous- and organic phase catalytic systems for reducing phenolic compounds into alkanes have been reported.^{4,5} However, the HDO of phenols in aqueous media is thermodynamically disfavoured and additionally leads to the deactivation of heterogeneous catalysts due to the formation of carbon deposits on the catalysts' surface. These factors contribute to severe reaction conditions, resulting in high-energy consumption, even for the simplest compound, phenol. Since cyclohexanol is stable in aqueous solutions below 200 °C,^{6,7} the formation of cyclohexane usually requires reaction temperatures above 200 °C, even in presence of a noble metal catalysts and under acidic conditions.^{8–10} At reaction temperatures below 200 °C in aqueous media, the main products are cyclohexanol and cyclohexanone.^{7,11,12} Noble metal catalysts in organic solvents give the desired selectivity

below 150 °C,^{13,14} but avoiding organic solvents would be advantageous. As an alternative to organic solvents, supercritical carbon dioxide (scCO₂) has been used as a reaction medium for the HDO of phenol, which also allows lower reaction temperatures. Drawbacks for an industrial application are the modest preference of cyclohexane and involvement of high pressures.^{15,16} Therefore, other solvents for the HDO of phenols are required, which ideally operate at low temperatures (<100 °C) and near-ambient pressures (1.0 MPa).

Ionic liquids (ILs) have been extensively investigated as solvents for the transformation of biomass into value-added products.^{17–19} In downstream processes, the alkane products are essentially insoluble in the ILs, whereas the phenolic substrates are soluble. This is a clear advantages of a pseudo-homogeneous system which affords a biphasic system as the product is formed, shifting the reaction equilibrium towards to the product.

The NP/IL catalytic system is versatile on the hydrogenation processed.^{20–22} The reaction temperature for the HDO of phenol can be as low as 130 °C,^{23–26} and clearly it would be advantageous to operate the reaction at lower temperatures. In our study we evaluated the performance of Pt NPs dispersed in ILs as a catalytic systems for the HDO of phenol (an abundant model/component of bio-oil).²⁷ The NPs were generated *in situ* and directly employed in the HDO of phenol under 1.0 MPa H₂ at 60 °C. To the best of our knowledge this reaction has not previously been achieved under such mild reaction conditions. After optimization of the reaction conditions, the system was used to transform a series of more complex phenolic compounds and to the hydrogenolysis of C–O bonds.

Results and Discussion

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A series of Pt NP solutions were prepared from H_2PtCl_6 in [Emim]NTf₂ or [Emim]NTf₂ containing a second IL, Lewis acid or Brønsted acid, using H_2 as the reductant (see Table 1). In most cases the NPs form rapidly, as evidenced by the solution turning black, which is as expected as [Emim]NTf₂ is an excellent stabilizer for metal NPs.^{28,29} TEM analysis of Pt NPs extracted from the [Emim]NTf₂ IL reveals NPs with an average diameter of

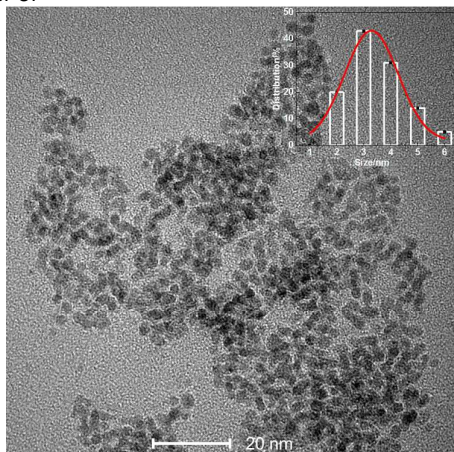


Fig. 1 TEM micrograph and histograms showing the size distribution of Pt NPs prepared in [Emim]NTf₂

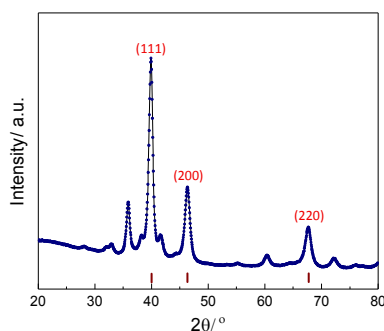


Fig. 2 TEM micrograph and histograms showing the size distribution of Pt NPs prepared in [Emim]NTf₂

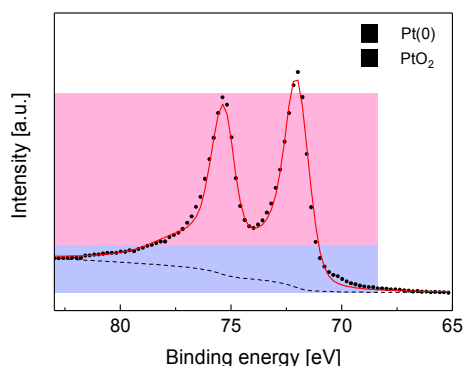


Fig. 3 TEM micrograph and histograms showing the size distribution of Pt NPs prepared in [Emim]NTf₂

3.4 nm (Fig. 1). TEM images of the Pt NPs isolated from all the other solutions are shown in the SI Fig. S5-8. The average

diameter of Pt NPs in the [Emim]NTf₂ containing a second IL are all between 3.4 nm to 3.9 nm which shows the stability of [Emim]NTf₂ as the stabilizer for the Pt NPs. With only [Bmim]PF₆, the mean diameter of Pt NPs is 5.5 nm, and that is larger than the one in [Emim]NTf₂. The precursors PtO₂ or Pt₂(dba)₃ (dba = bis-dibenzylidene acetone) yield upon reduction in [Bmim]PF₆ at 75 °C Pt NPs with an average size of 2.5 nm without any large agglomerates.^{20,21} The precursors can either react with hydrophobic or hydrophilic regions of imidazolium ILs and the different reaction temperatures that are the possible explanations for obtaining Pt NPs of various size.³⁰⁻³²

The XRD data shown in Fig. 2 indicate that the crystal type of the Pt NPs prepared in [Emim]NTf₂ is face-centered cubic (fcc), based on the diffraction peaks at 111, 200 and 220. Using the Scherrer equation the mean diameter of Pt NPs is estimated to be approximately 5.4 nm from the 220 diffraction line, somewhat larger than the value obtained from TEM. From the XPS data (Fig. 3), the Pt NPs have two valence states, the expected reduced state, Pt(0), and a lesser amount of an oxidized state, i.e. PtO₂. The full XPS pattern shows the presence of O and F, implying interactions between the IL and Pt NPs (SI, Fig. S10).

Conversion of phenol

We evaluated the catalytic performance of the NP/IL systems in the HDO of phenol under 1.0 MPa of H_2 at 60 °C, for 15 h (Table 1). The reaction is highly depending on co-IL or acid used, although in most cases cyclohexane is obtained as the main product, accompanied by other C₆-monoproducts such as cyclohexanol and cyclohexanone. Note that in the absence of Pt no reaction is observed (Table 1, entry 1). Cyclohexene is obtained in some of the reactions, i.e. those with a co-IL with a PF₆⁻ or BF₄⁻ anion (Table 1, entries 3, 4, 8, 13, 15, 16). Isolation of cyclohexene is probably due to its low solubility in the IL reaction medium, thus, once it is formed it is removed from the vicinity of the Pt NP catalyst and is not hydrogenated further. Differences in the solubility of substrates and partially hydrogenated products in ILs have previously been used to control reaction selectivity.^{24,33,34} In addition, C₁₂-dimers were detected in the reaction mixture, albeit at low yields. Details of the C₁₂-dimers are provided in Table S1 (Supporting Information). The formation of dimers presumably results from a stabilizing effect by the ILs on cyclohexyl cations which subsequently undergo dimerization via electrophilic aromatic substitution or aldol condensation reactions.^{23,35}

The Pt NP/[Emim]NTf₂-[Bmim]PF₆ system affords cyclohexane in highest yield, i.e. 86% together with 8% cyclohexene (Table 1, entry 3). The activity of this system is also superior to that of the well-studied heterogeneous catalysts Pt/C and Pt-Ni₂P/C (Table S4, entries 4,5). The Pt-Ni₂P/C was synthesised followed by the reported method.³⁶ The combination of the two hydrophobic anions, Tf₂N⁻ and PF₆⁻, is critical and they presumably enhance the dehydration of cyclohexanol, facilitating the elimination of the water by-product. In [EMIM]OTf at 60 °C, NPs are not

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Table 1 Yields of products and conversion of phenol over Pt NPs prepared in [Emim]NTf₂ with a second IL, Lewis acid or Brønsted acid

	ILs2/LA/BA	Con (%)	Selectivity (%)					DOR	TOF
			-ane	-ene	-nol	-one	Di		
1 ^a	[Bmim]PF ₆	0	0	0	0	0	0	0	
2	-	100	45	0	53	1	1	45	
3	[Bmim]PF ₆	100	86	8	0	0	6	94	
4 ^b	[Bmim]PF ₆	100	82	8	1	0	9	91	
5	[Bmim]OTf	49	54	0	27	19	0	27	
6 ^b	[Bmim]OTf	0	0	0	0	0	0	0	
7 ^{b,c}	[Bmim]OTf	52	59	0	10	31	0	31	
8	[Bmim]BF ₄	100	52	19	18	0	11	72	
9 ^b	[Bmim]BF ₄	50	46	0	31	23	0	28	
10	[Bmim]Cl	0	0	0	0	0	0	0	
11 ^c	[Bmim]Cl	45	45	0	21	34	0	20	
12	[Emim]OAc	0	0	0	0	0	0	0	
13	[N(CH ₃) ₄]PF ₆	100	44	2	47	0	7	46	
14	[N(CH ₃) ₄]ClO ₄	100	50	0	41	6	3	50	
15	[Bmmim]PF ₆	100	61	13	17	3	6	84	
16	[Bmpy]PF ₆	75	63	5	18	5	12	52	
17	AlCl ₃	100	37	0	45	6		39	
18	ZnCl ₂	100	43	0	36	0	21	44	
19	Cu(OTf) ₂	10	71	12	0	0	17	9	
20	H ₃ PO ₄	100	56	0	42	0	2	56	
21	HCl	55	45	0	39	15	1	25	

ILs2: [Bmim]PF₆; LA: Lewis acid; BA: Brønsted acid; Con: conversion; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; Di: total dimers; DOR: deoxygenation rate. TOF: [mol cyclohexane]/[mol Pt][hour] and d: TOF for exposed metal³⁷

a: without Pt; b: without [Emim]NTf₂; c: 130 °C

Reaction conditions: [Emim]NTf₂ (2.0 g), ILs2/LA/BA (0.5 g/0.2 g/0.2 g), H₂PtCl₆ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H₂, 60 °C, 15 h. Reproducibility of the results: ±5 %.

[Bmim]OTf: 1-Butyl-3-methylimidazolium trifluoromethanesulfonate; [Bmim]BF₄: 1-Butyl-3-methylimidazolium tetrafluoroborate; [Bmim]Cl: 1-Butyl-3-methylimidazolium chloride; [Emim]OAc: 1-Ethyl-3-methylimidazolium acetate; [N(CH₃)₄]PF₆: Tetraethylammonium hexafluorophosphate; [N(CH₃)₄]ClO₄: Tetramethylammonium perchlorate; [Bmmim]PF₆: 1-n-butyl-2,3-dimethylimidazolium hexafluorophosphate; [Bmpy]PF₆: 1-butyl-4-methylpyridinium hexafluorophosphate.

formed and the phenol is not converted (Table 1, entry 6), whereas at higher temperature of 130 °C, NPs formation takes place and some conversion of the substrate is observed (Table 1, entry 7).

Influence of the IL ions

ILs are known to play a crucial role in dehydration step of HDO reactions, with performance of ILs is related to their acidity and hydrophobicity.¹⁸ Hence, different combinations of cations and anions were evaluated (Table 1, entries 3-11). The performance of the ILs increases in the order: [Bmim]PF₆ > [Bmim]BF₄ > [Bmim]OTf >> [Bmim]Cl ~ [Emim]OAc. Essentially, the IL with the most hydrophobic anion, PF₆⁻, leads to the highest activity in combination with [Emim]NTf₂. An obvious

sign for that is that the ILs solutions (Table 1, entries 10, 12. [Bmim]Cl and [Emim]OAc) with the dissolved metal salt remain yellow, which indicates that no Pt NPs were formed and further, the conversion of phenol did not occur. The non-nucleophilic anions, Tf₂N⁻ or PF₆⁻, facilitate the formation of Pt NPs, since they interact only weakly with the Pt(IV) salt precursor, allowing reduction to take place, as noted previously.³⁸ Moreover, in keep with other studies, non-nucleophilic anions enable catalysts, surface of NP, as they can be displaced by the substrates more easily than strongly nucleophilic anions.^{39,40}

Since both, Tf₂N⁻ and PF₆⁻, are hydrophobic and weak nucleophiles, it remains unclear why one outperforms the

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Table 2 Yields of products and conversion of substituted phenol over Pt NPs in ILs

	Substrates	Con (%)	Sel (%)				TOF
			-ane	-ene	-nol	-one	
1	Benzene	100	93	7	0	0	3.1
2	Catechol	100	85	4	8	0	2.8
3	Resorcinol	100	85	5	2	0	2.8
4	Pyrogallol	100	83	8	2	0	2.8
			-ane	-ene	-nol		
5	Anisole	100	56	3	0	40	1.8
6	Guaiacol	38	62	5	0	21	0.8
			-ane	-ene	-nol		
7 ^a	Diphenyl ether	100	50	10	15	25	1.7
8	Diphenyl ether	100	68	11	6	13	2.3

Con: conversion; Sel, selectivity; -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; Di: total dimers; DOR: deoxygenation rate; TOF: [mol main product]/[mol Pt][hour]

Reaction conditions: [Emim]NTf₂ (2.0 g), [Bmim]PF₆ (0.5 g), H₂PtCl₆ (0.01 mmol), substrate (0.5 mmol), 1.0 MPa H₂, 60 °C, 15 h. Reproducibility of the results: ±5 %.

^a: 40 °C.

other. However, Katsyuba *et al.* revealed that the PF₆⁻ anions form strong hydrogen bonds with the phenolic –OH groups on phenol,⁴¹ which in consequence activates C–O bonds and facilitates hydrogenolysis. Another reason could be the formation of HF via partial decomposition of PF₆⁻ in the presence of water,⁴² which should, as a Brønsted acid, facilitate the dehydration step. The ESI-MS spectrum of the mixture after the reaction is shown in Fig. S11. The peak found at 100.96 correspond to the anion PO₂F₂⁻ (calc. 100.96), which would be the expected product of PF₆⁻ after hydrolysis. Evaluation of a series of PF₆⁻-based ILs shows that the cation has little impact on the reaction Table 1, entries 13–16). Catalytic activity increases in the following order Bmim⁺ > Bmmim⁺ > N(CH₃)₄⁺ > Bmpy⁺. The small difference (< 25%) may be related to the hydrogen-bonding ability of the cation, with the acidic 2-proton in the Bmim⁺ cation helping to activate the substrate.⁴³

Evaluation of acids as co-catalysts

The dehydration of cyclohexanol, which is apparently the rate-determining step,^{44,45} usually proceeds more efficiently under acidic conditions. In addition, in the mechanism the keto/enol step is believed to require a considerably larger concentration of acid sites compared to the available metal sites for hydrogenation.⁶ Therefore, we evaluated Lewis and Brønsted acid additives in the Pt NP/[Emim]NTf₂ catalytic system (Table

1, entries 17–21). None of the acids led to superior performances to the system containing [Bmim]PF₆. This implies that the Pt NP/[Emim]NTf₂-[Bmim]PF₆ system is sufficiently acidic so that the addition of further acid has little impact on the reaction. The reduction of the H₂PtCl₆ results in the generation of HCl and consequently an intrinsically acid IL solution. Indeed, using other Pt salt precursors that do not generate acid upon reduction, e.g. PtO₂, K₂PtCl₄, results in lower catalytic activities (Table S4, SI).

Reaction optimisation

The Pt NP/[Emim]NTf₂-[Bmim]PF₆ system was further optimized. The HDO of phenol to cyclohexane was executed within a temperature range from 25 °C to 100 °C, H₂ pressures ranging from 0.1 MPa to 10.0 MPa and reaction times from 5 h up to 25 h. Remarkably, even at room temperature (25 °C) the system catalyzes the HDO of phenol (Fig. 4) at an acceptable rate. As the temperature is increased the yield of cyclohexane increases, reaching 96% at 100 °C.

The hydrogenation products of phenol in Pt/ILs catalytic system is plotted in Fig. 5 as a function of time at 60 °C and 1.0 MPa H₂. The curve corresponding to the conversion of the substrate indicates that the Pt NP catalyst is generated in situ and consequently is not ideal for full analysis. In a first step cyclohexanone and cyclohexanol are formed, then the ketone are rapidly hydrogenated to cyclohexanol. Subsequently,

cyclohexanol dehydration directly leads to cyclohexene (acid catalysis) and ultimately metal-catalysed cyclohexene hydrogenation yields cyclohexane. Thus, cyclohexane became the major product with 86% selectivity.

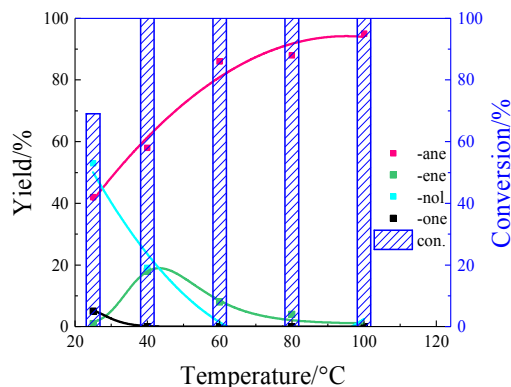


Fig. 4 Yields of products and conversion of phenol over Pt NPs prepared in ILs ([Emim]NTf₂ (2.0 g), [Bmim]PF₆ (0.5 g), H₂PtCl₆ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H₂, 15 h. Reproducibility of the results: ±5 %.) solid points: experiment data, line: curve for visualize tendency. -ane: cyclohexane; -ene: cyclohexene; -nol: cyclohexanol; -one: cyclohexanone; con.: conversion.

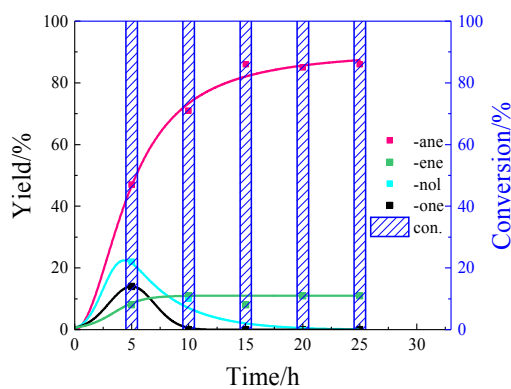


Fig. 5 The products distributions and conversion of phenol over Pt NPs prepared in ILs ([Emim]NTf₂ (2.0 g), [Bmim]PF₆ (0.5 g), H₂PtCl₆ (0.01 mmol), phenol (0.5 mmol), 1.0 MPa H₂, 60 °C. Reproducibility of results is ±5 %.) solid points: experiment data, line: curve for visualize tendency.

The catalytic activity was also studied as a function of the H₂ pressure (Fig. 6). Even at 0.1 MPa H₂ the substrate was fully transformed although the selectivity to cyclohexane is lower than that observed at 1.0 MPa hydrogen pressure. At a pressure of 10.0 MPa only a slight increase in selectivity towards cyclohexane was observed. Although hydrogen gas solubility is low in ILs the rate of mass transfer of hydrogen into ILs seems to be fast,⁴⁶ showing why the hydrogen pressure has only minor influence on the reaction.

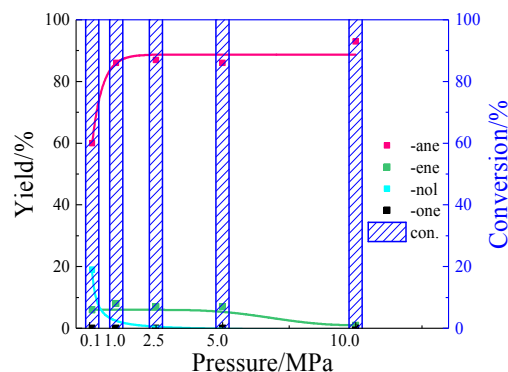


Fig. 6 Yields of products and conversion of phenol over Pt NPs prepared in ILs ([Emim]NTf₂ (2.0 g), [Bmim]PF₆ (0.5 g), H₂PtCl₆ (0.01 mmol), phenol (0.5 mmol), 60 °C, 15 h. Reproducibility of the results: ±5 %.) solid points: experiment data, line: curve for visualize tendency.

Substrate scope

A series of more complex substrates (Fig. 7) with one or more hydroxyl or methoxy groups were evaluated. Catechol, for example, is one of the major components found in lignin depolymerisation products and bio-oil.^{47,48} Aromatic alcohols with two or more hydroxyl groups such as catechol, resorcinol or pyrogallol were completely converted, showing a high selectivity for cyclohexane (Table 2). The number and position of phenolic hydroxyl groups does not reduce the catalytic activity of the Pt NP/[Emim]NTf₂-[Bmim]PF₆ system.

With substrates with methoxy substituents, the selectivity of the HDO reaction decreases substantially. For example, anisole afforded two main products, i.e. cyclohexane and cyclohexyl methyl ether. The reductive removal of methoxy groups is less effective than dehydration of cyclohexanol. Since the bond dissociation energy of C-O for methoxy groups is with 290 kJ/mol considerably higher than 190 kJ/mol for phenolic hydroxyl groups, their elimination is also more demanding.⁴⁹ Guaiacol, which is a major fraction in bio-oil and a typical lignin-derived monomer, contains three different types of C-O bonds. Moreover, the steric hindrance exerted by methoxy groups is more pronounced than for hydroxyl groups. As a result, the conversion and selectivity for cyclohexane of guaiacol are lower than for phenol.

The Pt NP/[Emim]NTf₂-[Bmim]PF₆ system was also evaluated as a catalyst for the hydrogenolysis of diphenyl ether (DPE), which possesses a very strong C-O bond. Cyclohexane was obtained in 68% yield, the main by-product is the aliphatic ether oxydicyclohexane.

In summary, the Pt NP/[Emim]NTf₂-[Bmim]PF₆ systems is an excellent catalyst for the HDO of bio-oil type compounds. The system operates under remarkable mild conditions and is stable allowing several recycling (SI, Table S3). The selectivity

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towards cyclohexane remains high in recycling experiments only the conversion of phenol progresses more tempered. The observed slow-down of catalytic activity might be caused by aggregation processes of NPs during the reaction. After three catalytic cycles, the size of Pt NPs increased to 4.3 nm, and TEM image of aggregated Pt NPs is showed in the Fig. S4. The current systems leaves room for optimization, especially stable and high TOFs throughout multiple re-uses of the catalyst is one of the most appealing starting-points for future work.

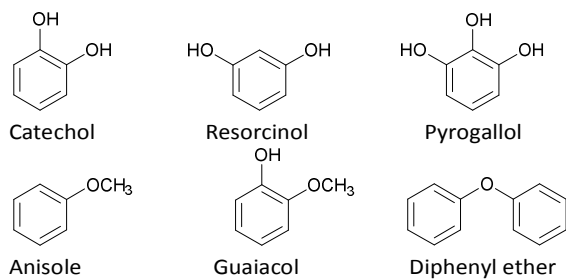


Fig. 7 Substrates employed

Experimental

Materials

The ILs used in this study were dried under vacuum at 60 °C for 24 h before use. The ILs were characterised using NMR spectroscopy recorded by Bruker 400 MHz instrument (see Supporting Information). Other chemicals, including phenol (CP, Acros), guaiacol (CP, Fluka), diphenyl ether (CP, VWR International SA) and substituted phenols were obtained from Acros or Sigma-Aldrich and used without further purification.

Pt NPs characterisation

The Pt NPs were isolated by centrifugation (5000 rpm) for 15 minutes, then were washed by dichloromethane (3 × 5 mL) and ethanol (3 × 5 mL). The final re-suspended ethanolic solution was ultra-sonicated for 1 h. Subsequently, the ethanol suspension of nanoparticles was deposited on a carbon film coated copper grid and then examined by trans-mission electron microscopy (TEM). (FEI Talos, operated at 200 keV).

Catalyst Testing and Product Analysis

The experiments were performed in a 45 mL batch reactor. For a typical experiment, the reactor was loaded with substrate (0.5 mmol), H₂PtCl₆ (0.01 mmol), [EMIM]NTF₂ (2.0 g) and [BMIM]PF₆ (0.5 g). After purging with H₂ (1.0 MPa) three times, the mixture was stirred at 700 rpm and heated to 60 °C for 15 h. Thereafter, the autoclave was allowed to cool to room temperature and the H₂ gas was released. Upon that, the products were extracted with 8 ml diethyl ether. The final products were identified by GC-MS using a Agilent 7890B Gas Chromatograph equipped with an Agilent 7000C GC/MS triple quad detector and a capillary column from Agilent (30 m ×

0.25 mm × 0.25 μm) with a connected flame ionization detector (FID) for quantification.

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Description for the graphical abstract:

Hydrodeoxygenation of bio-derived phenols under mild conditions with platinum nanoparticles in situ synthesized in the ionic liquid



64x42mm (300 x 300 DPI)