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# ARTICLE

Received 00th January 20xx,

Journal Name

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

## Conversion of Lignin Model Compounds at Mild Conditions in Pseudo-Homogeneous Systems

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To produce basic chemicals from lignin, depolymerization and removal of oxygen from lignin through C-O cleavage and hydrodeoxygenation (HDO) are crucial steps. In this study, a novel catalyst system, pseudo-homogeneous catalyst system, consisting of uniformly stabilized noble metal nanoparticles (NPs) in ionic liquids is developed for the selective reductive cleavage of C-O and HDO. Phenol and guaiacol as lignin monomer model compounds are investigated to get an insight into the possible HDO pathway, meanwhile, dimeric model compounds, such as diphenyl ether, benzyl phenyl ether, are studied for the cleave C-O bonds between aromatic units. Four types of NPs including Pd, Pt, Rh, Ru were in-suit synthesized and well-distributed in ILs without aggregation. These catalytic systems displayed almost 100% conversion for various monomer and dimer lignin model compounds at 130 °C and were recycled several times without lossing activity. The catalytic selectivity of metals for HDO/C-O cleavage normally decreases with the order of Pt > Rh ~ Ru >> Pd that is similar with the order of NPs size Pd >> Pt > Rh ~ Ru. With mean diameter of 5.6 nm, Pt NPs in [Bmim]PF<sub>6</sub> is identified as the best catalytic system for the transformation of lignin monomers and dimers model compounds with almost 100 % conversion and maximum 97 % selectivity.

#### Introduction

Since currently over 95% of organic chemicals are derived from petroleum,<sup>1</sup> the depletion of petroleum may gradually lead to energy and chemicals crises. Thus, to find new alternatives for petroleum has become one of the most urgent tasks. Lignin, as the second most abundant biomass polymer on the earth and the only large-volume renewable aromatics feedstock as well, accounts for 10 to 30 %<sup>2, 3</sup> by dry weight of biomass while up to 40 %<sup>4, 5</sup> by energy and is considered as one of the most promising bulk feedstocks to produce platform chemicals. Nonetheless, most of them from the pulp and paper industry are underutilized feedstocks, which are just limited to low value fuels.<sup>6, 7</sup> Furthermore, more and more lignin will be generated as the bio-refineries which is based on lignocellulosic biomass emerging in a large scale.8,9 Efficient conversion of lignin not only makes contribution to the petroleum crisis and economic viability, but also relieves the solid waste disposal problem. Compared with lignin conversion by a single step, a two-step conversion strategy, which consists of depolymerisation and

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There are still two challenges in the two-step lignin conversion strategy: (1) developing an efficiency catalyst that depolymerises lignin through cleavage of linkages to produce small basic chemicals; (2) finding a suitable medium that dissolves lignin and facilitates the interaction between the dispersed lignin and catalyst.<sup>6</sup> Due to the over-functionalized structure,<sup>5</sup> depolymerisation of lignin into small molecules is a tough synthetic problem for a long time.<sup>13</sup> Among all the linkages of lignin, C-O-C bonds (account for two-thirds to three-quarters of all the linkages) and C-C bonds should be cleaved through depolymerisation.<sup>14</sup> Although C-O-C bonds are relative readily to be cleaved than C-C bonds, the aryl C-O

Table 1 Types and Frequencies of Inter-Subunit Linkages in Softwood and Hardwood Lignins (number of linkages per 100 C9 units) <sup>15-20</sup>

	Linkage	Bond dissociation energy/ kJ/mol	Softwood Lignin /%	Hardwood Lignin /%
	β-0-4	226-303	45-50	65
	α-0-4	156-203	6-8	-
	β-5	-	9-12	6
	4-0-5	346	4-8	1.5

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<sup>&</sup>lt;sup>+</sup>Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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bonds cleavage is still a significant barrier because of the relative high bond dissociation energy with the highest 346 kJ/mol as shown in Table 1.<sup>21, 22</sup> Typically, the hydrogenolysis of aryl C-O bonds is operated at high temperature (>250 °C) and high H<sub>2</sub> pressure (>3 MPa) over heterogeneous catalysts.<sup>10,</sup> <sup>23</sup> After depolymerisation, upgrading of monomers and dimers through hydrogenation or HDO at mild conditions to remove the additional groups (e.g. hydroxyl, methoxyl) is another remaining challenge.24 The conventional (sulfide based) heterogeneous catalysts tend to be deactivated rapidly and are harmful to the environment by employing sulfur.<sup>25</sup> The recently emerged bifunctional catalysts, coupled hydrogenation site with dehydration site, showed good performance in HDO at high temperature (>200 °C) and high H<sub>2</sub> partial pressure (3 -20 MPa) in aqueous phase.26 However water would inhibit the deoxygenation when the oxygen is removed as the form of H<sub>2</sub>O. Furthermore, water is an anti-solvent of lignin which impedes the dissolution.<sup>27, 28</sup>

With the improvement based on the bifunctional catalysts, ionic liquids (ILs) as the substitution of water are not only environmentally benign but also serve as good catalysts for hydrolysis of C-O bonds of lignocellulose.<sup>29-31</sup> Meanwhile, ILs are regarded as green solvents and are more effective in lignin dissolution than other solvents even at room temperature.<sup>6, 32-35</sup> Nevertheless, to date, examples of lignin-based chemical production in ILs remain scarce.<sup>36-38</sup> On the other hand, the noble metals are known to all as highly active catalysts in both hydrogenation<sup>39, 40</sup> and C-O activation.<sup>14, 41</sup> Owing to structural directionality (IL effect), self-organization and electrostatic stabilization effect, nanoparticles (NPs) are stable with high activity in ILs.42-44 The perfect combination of ILs and NPs was originally applied in olefins hydrogenation as pseudohomogeneous catalyst,42 and then it was widely used in hydrogenation, oxidation and C-C coupling.45-48

Herein we describe a pseudo-homogeneous catalytic system (NPs/IL-H<sub>3</sub>PO<sub>4</sub>) for the HDO and C-O bonds cleavage, and this catalytic system combines the virtues of homo- and heterogeneous catalysts, namely this catalyst is able to access the reactive sites in lignin and to be recycled easily after the reaction as well. The NPs were synthesized by reducing the metal salt in-situ in ILs, followed by directly used in the HDO/C-O bond cleavages reactions. These reactions were mimicked by lignin dimers model compounds: 2-phenylethyl phenyl ether ( $\beta$ -O-4), benzyl phenyl ether ( $\alpha$ -O-4), etc. Since less research has been done in lignin conversion after depolymerisation<sup>32</sup>, these studies about the conversion of phenol and guaiacol as the lignin monomers model compounds are also significant. It was marvellous that most of the lignin model compounds were completely converted at the mild reaction temperature 130 °C, while the traditional heterogeneous catalysts only showed little activity. To find out the impact of anions and the length of the alkyl chain of cations of ILs on the activity and selectivity of reactions, a series of ILs have been tested. Lastly, noble metal catalysts, Pd, Pt, Rh and Ru, were screened for HDO/C-O bond cleavages and the most active one was evaluated in the recycling test.

#### Experimental

#### 2.1 Materials

The ILs used in this study, including 1-allyl-3-methylimidazolium N-bis- (trifluoromethanesulfonyl) imidates ([Amim]NTf<sub>2</sub>), 1-n-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF<sub>6</sub>), and 1-n-butyl-3-methylimidazolium tetrafluoroborates ([Bmim]BF<sub>4</sub>) etc, were dried under vacuum at 80 °C for 24 h before used. The purity of IL was proved by the <sup>1</sup>H-NMR (Figure S1-S6). Other chemicals, including phenol (CP), guaiacol (CP), diphenyl ether (CP), 2-phenylethyl phenyl ether, (>98.0 wt%), benzyl phenyl ether (>97.0 wt%), and benzofuran (>99.0 wt%) were obtained from J&K or Sigma-Aldrich and used without further purication. The dealkalized lignin (65.85% C, 7.01% H, 2.43% N, 24.03% O and 0.62% S by difference) was purchased from J&K. Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>6H<sub>2</sub>O), ruthenium chloride hydrate (RuCl<sub>3</sub> 3H<sub>2</sub>O), palladium chloride (PdCl<sub>2</sub>), rhodium chloride hydrate (RhCl<sub>3</sub> 3H<sub>2</sub>O) were purchased from J&K with 99.9% purity. H<sub>2</sub> was received from Beijing Beiwen Gas Factory, and the purity was 99.999%.

#### 2.2 Experimental

#### 2.2.1 Organosolv Lignin Synthesis

The real wood sawdust was screen by 120 mesh sieve, and then it was extracted by ethanol–water (1:1) for 3 h at 180 °C. After filtration, water was added into the filtrate to precipitate organosolv lignin. After filtration again, the solid was dried in vacuo for overnight. The composition organosolv lignin was characterized by Elemental analysis (65.68 % C, 6.48 % H, 3.94 % N, 23.09 % O and 0.76% S by difference) and FTIR (Figure S7), and the molecular weight distribution of the obtained organosolv lignin was determined by gel permeation chromatography (GPC) (Figure S8).

#### 2.2.2 Nanoparticles Formation and Reactions

In a typical experiment, the solution of chlorate salts of noble metal (0.01 mmol) with ionic liquid (2 g) and methanol (1 g) was stirred at room temperature for 15 min. The volatiles were then removed under reduced pressure (0.1 bar) at 75°C for 2 h in a rotary evaporator. The lignin model compounds (1 mmol) or Organosolv lignin (0.1 g), also called substrates, and H<sub>3</sub>PO<sub>4</sub> (0.15 g) were added into a autoclave with a teflon cell. The autoclave was sealed and purged with hydrogen for three times before pressurized with 5 MPa H<sub>2</sub> at room temperature. Then the autoclave was placed in a heating block maintained at 130 °C for 10 h with a stirring of 800 rpm. The products were analyzed by gas chromatography-mass spectrometer (GC-MS). GC-MS analyses were performed in an Agilent 6890N/5975B GC-MS equipped with a HP-5MS capillary column (25 m × 0.25 mm, using He as carrier gas). Samples were tested with split ratio of 30:1 and an injection volume of 0.4 µL. The GC oven was programmed to begin with 40 °C for 3 min, and then raised with the rate of 10 °C/min until the temperature reached 270 °C and held at the final temperature for 2 minutes giving a total run time of just over 28 min.

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#### 2.2.3 Sample Preparation and NPs Characterization

The NPs were isolated by centrifugation (5000 rpm) for 15 minutes, and then washed with dichloromethane ( $3 \times 5 \text{ mL}$ ) and ethanol ( $3 \times 5 \text{ mL}$ ). The final solution was ultra-sonicated for 1 h. The ethanol suspension of nanoparticles was deposited on a copper grid coated by carbon film and then used in transmission electron microscopy (TEM) test. The morphology and size of isolated NPs were observed by TEM (JEM 2100-F (UHR)) operated at 200 keV, and scanning electron microscope (SEM) (SU8020) examination which was operated at 15 keV.

Before the X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) tests, the isolated NPs was dried under reduced pressure for 8 h. XPS data were recorded on a ESCALAB 250Xi operated at Pass Energy 20.0 eV for signal element and 100.0 eV for whole survey, while the XRD instrument was collecting data by Smartlab (9) on a 2D image plate were integrated between 20° and 90°  $2\theta$  with a step size of 0.05° and time of 1 s per step.

#### **Results and discussion**

#### 3.1 Characterization of NPs

#### 3.1.1 Active Component of NPs

From the XPS results, all the NPs have two valence states, reduced state and small amount of oxidized state as shown in Figure 1. The present of O suggests that NPs surface is susceptible to oxidation in air, and the oxidized surface may also enhance the stability of NPs.<sup>49</sup> Undoubtedly, the active phase of NPs is the reduced state metal. The presence of F

indicated in the Figure S9-S12 is one of evidences for the relatively strong interaction between ILs and the surface of metal NPs even after isolation.<sup>46</sup> The scanning electron microscopy with energy dispersive X-ray (SEM-EDX) (Figure S13-S15) data is consistent with XPS patterns showing the existence of O and F as well.



Figure 1 XPS of the prepared NPs with [Bmim]PF<sub>6</sub> showing the 3d region with the fitting results, (a) Pd NPs, (b) Pt NPs, (c) Rh NPs, (d) Ru NPs (The C 1s signal was a contribution from the carbon tape which was unavoidable during the test)



Figure 2 TEM Micrographs and histograms showing the size distribution of NPs prepared in [Bmim]PF<sub>6</sub> before reaction, (a) Pd NPs, (b) Pt NPs, (c) Rh NPs, (d) Ru NPs

DOI: 10.1039/C5GC03121D

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(a) Pd (b) Pt (c) Rh (c) Rh (c) Rh (d) Ru (d

Figure 3 TEM Micrographs and histograms showing the size distribution of NPs prepared in [Bmim]PF<sub>6</sub> after reaction, (a) Pd NPs, (b) Pt NPs, (c) Rh NPs, (d) Ru NPs

#### 3.1.2 Mean Diameter of NPs

The size of NPs has strong influence over the activity and selectivity of catalysts.<sup>50-52</sup> The mean sizes of NPs in this study were determined by TEM in randomly selected areas and based on at least 150 particles. Since these NPs are isolated and exposed to the air, the oxidized layer may enlarge the particle size. Nonetheless, the mean diameters of these isolated particles have been determined by TEM and usually were quite close to those obtained from the nanoparticles dispersed in the ILs as others reported.<sup>46</sup> Representative TEM micrographs with their corresponding histograms of the obtained four types NPs before and after reaction are presented in Figure 3, while the mean diameter of each NPs is listed in Table 2. The mean diameter decreases with the order of Pd >> Pt > Rh > Ru. The solubility of the metal precursor influences the size of the metal NPs.53 The precursor of the Pd, PdCl<sub>2</sub>, is difficult to be dissolved in ILs and the formed Pd NPs have the largest size. To obtain a better understanding of the recycle ability of NPs, the spent catalysts were characterized using TEM as well. Before the reactions, the NPs are uniformly dispersion with less aggregation, while these trend to aggregate. The differences in the mean diameters of NPs between before and after reactions are usually less than 1 nm, which indicates the high possibility of recycling and reusing.

### 3.1.3 Crystal Form Selected Area Electron Diffraction (SAED) and XRD

The crystal form of each metal is determined by selected area electron diffraction (SAED) in Figure 4. The electron diffraction rings demonstrated that the crystal forms of Pd and Pt NPs are polycrystals with preferred crystal orientations, while Ru and Rh NPs are polycrystals without preferred crystal orientations.

The XRD data in Figure 5 confirmed the crystalline types of NPs. Pd, Pt and Rh NPs are face-centered cubic (fcc), while Ru NPs are hexagonal structure. Although the estimated mean sizes of these NPs from XRD in Table S3 are larger than TEM



Figure 4 Theoretical (right) and experimental (left) electron diffraction rings, (a) Pd NPs, (b) Pt NPs, (c) Rh NPs, (d) Ru NPs

Table 2 Mean diameter of noble metal NPs

Mean Diameter/nm	Pd	Pt	Rh	Ru	
Before Reaction	34.1	5.6	3.4	2.4	
After Reaction	35.5	6.7	3.8	2.8	

results, the order of diameters is the same, Pd > Pt > Ru > Rh. The difference could due to the limitation of Scherrer equation in small size NPs less than 5 nm. Another reason is the small amount of test samples that leads to the random error.

#### 3.2 Conversion of Lignin and Model Compounds

The cleavages of C-O bonds and HDO performance of pseudohomogeneous catalytic systems are investigated through lignin monomers and dimers model compounds listed in Scheme 1.



Figure 5 X-ray diffraction pattern of the isolated NPs dispersed in [Bmim]PF<sub>6</sub>, (a) Pd NPs, (b) Pt NPs, (c) Rh NPs, (d) Ru NPs. Experimental data (black), refined fitting line (blue line) and difference between the experimental values and the fitting model (red line)



Scheme 1 Lignin monomers and dimers model compounds (a) phenol; (b) guaiacol; (c) diphenyl ether (4-O-5); (d) Benzyl phenyl ether ( $\alpha$ -O-4); (e) 2-phenylethyl phenyl ether ( $\beta$ -O-4); (f) Benzofuran ( $\beta$ -5)



Figure 6 Yield of products from HDO of phenol over Pd, Pt, Ru, Rh NPs prepared in [Bmim]PF<sub>6</sub> and the result in Reference<sup>54</sup> (Left); Yield of different ILs over Pt (Right) (T: 130 °C, P: 5 MPa, 10 h; H<sub>3</sub>PO<sub>4</sub> 0.1 g, [Bmim]PF<sub>6</sub> 2g, Substrates/Pt=100)

#### A) Phenol

Figure 6 shows the yield and the corresponding product distribution from phenol under 5 MPa at 130 °C for 10 h. The main products of phenol are cyclohexane with small amount of bicyclohexyl as a side produce. The yield of cyclohexane with Pt NPs is the best among all the catalysts as shown in Figure 6 (Left). The catalytic activity of metal site for phenol hydrodeoxygenation to cyclohexane decreases with the order of Pt > Rh ~ Ru >> Pd. The effect of the length of the alkyl chain in cation is not very obvious in Figure 6 (Right), only the yield

of cyclohexane slightly declines when the length of the alkyl chain increased to six. However, the anions of ILs have great impact on the reaction, as phenol almost cannot be converted in [Bmim]BF<sub>4</sub>.

Ning Yan and co-workers reported the HDO of phenols in the Brønsted acidic ILs/NPs system.<sup>54</sup> The conversion and selectivity of phenol to cyclohexane were excellent but not good at the same time, the best selectivity to cyclohexane (98%) could only be obtained with a moderate conversion (48%). The results of our catalysts have little improvement with almost full conversion and 98% selectivity. It should be noted that the by-produce, bicyclohexane, was also found in our study as mentioned in few studies.<sup>55</sup>

The possible reaction pathways of phenol are depicted in Scheme 2, route 1 is the reaction pathway from phenol to main product cyclohexene while the route 2 and 3 are the possible reaction mechanisms of intermediate products, cyclohexyl phenol and cyclohexyl cyclohexanone. It is well known that noble metals (e.g. Pd, Pt) can activate  $H_{2,2}^{56-58}$  so almost all the hydrogenation steps are catalysed by noble metals. Moreover, the deoxygenation steps are promoted by acid sites. Through the Route 1, the main product, cyclohexane, is generated by full HDO. The phenol is converted to cyclohexanone first, and further hydrogenated to cyclohexanol, and then the subsequent deoxygenation yields cyclohexene. Finally, cyclohexene reacts with hydrogen to produce cyclohexane. The phenol is more apt to be dissolved in ILs, while cyclohexane tends to be separated from the ILs. This bi-phase phenomenal would facilitate the reactions.

A very interesting side produce, bicyclohexyl, was found in our experiments and has not been reported in ILs in previous papers. The mechanism of bicyclohexyl formation over heterogeneous catalysts has been studied in aqueous and solvent-free system.55 However, as far as we know, the mechanism study of this side reaction is still lacking with IL as the solvent. The possible reaction pathway of side produce bicyclohexyl is depicted in the Scheme 2, route 2 and 3. Through the electrophilic aromatic substitution of phenol (Route 2), cyclohexyl cation may recombine with phenol and then leads to the formation of cyclohexyl phenol.<sup>59-61</sup> Cyclohexanol combines with proton, then reacts with the ortho-C of phenol to produce cyclohexyl phenol. Then the cyclohexyl phenol is converted to bicyclohexyl by HDO which is similar to the conversion pathway of phenol. And 2-cyclohexyl cyclohexanone may be possible produced via aldol condensation (Route 3) between cyclohexanone and phenol.55, 62 Those reaction pathways may happen, because cyclohexyl cation is also stable in ILs.63 However, both Route 2 and 3 are difficult to occur. As Route 1 is much faster than other routes, the majority of the reactant is converted to cyclohexane, and the concentration of cyclohexanone and cyclohexanol are low. Besides, the low reactivity of cyclohexanone and cyclohexanol with proton also made the reactions of Route 2 and 3 remain difficult.

To verify these assumptions, the reaction was stopped at 3 h (the full reaction time was 10 h), and small amount of cyclohexyl phenol, cyclohexyl cyclohexanone and bicyclohexyl were observed. At the end of 10 h reaction, only bicyclohexyl

DOI: 10.1039/C5GC03121D Journal Name

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was detected. It is presumably that cyclohexyl phenol and cyclohexyl cyclohexanone were completely converted to bicyclohexyl. These small amount intermediate products are the evidences for the Route 2 and 3. As a further proof, cyclohexanol and cyclohexanone were used as substrates respectively at the same condition without noble metal. Both final mixtures contained bicyclohexyl, and cyclohexyl cyclohexanone was detected as well when the substrate was cyclohexanone. Some papers attributed their formation to the Pt-catalyzed recombination of (partially) hydrogenated monomeric species.<sup>64</sup> However, these recombination reactions also occurred in the absence of noble metal, so the present of proton should be the main reason for the formation of the side produce bicyclohexyl. It was reported that cyclohexanol would like to yield cyclohexene rather than cyclohexane when water was used as the solvent.<sup>26</sup> It is supposed that IL has better solubility of  $H_2$  than water. Therefore, cyclohexene can be hydrogenated to cyclohexane in spite of the absence of noble metal.



Scheme 2 Reaction pathway of phenol in the catalytic hydrogenation treatment

Figure 7 Yield of products from HDO of guaiacol over Pd, Pt, Ru, Rh NPs prepared in [Bmim]PF<sub>6</sub> and the result in Reference (Left); Yield of different ILs over Pt (Right) (T: 130 °C, P: 5 MPa,10 h; H<sub>3</sub>PO<sub>4</sub> 0.1 g, [Bmim]PF<sub>6</sub> 2g, Substrates/Pt=100) Compare with phenol, the -OCH<sub>3</sub> group has large impact in the HDO process. Guaiacol is converted to cyclohexane with a selectivity of 91% at full conversion when Ru as the catalyst.

Revited Rev

B)

'ield/%

Guaiacol

NPs/IL, H<sub>2</sub>PO

OCH<sub>3</sub> 130 °C, H<sub>2</sub>: 5 MPa, 10 h

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and ketone/enol isomerization, guaiacol may be converted into 2-methoxycyclohexanone. Reacting with hydrogen, 2methoxycyclohexanone is turned into methoxycyclohexanol. Then methoxycyclohexanol can be hydrolyzed to cyclohexanediole, and afterwards cyclohexanediole would be dehydrated into cyclohexanone very readily. It is speculated that the methoxycyclohexanol reaction pathway is first through acid-catalyzed hydrolysis to yield 1,2-cyclohexanediol and followed by the (acid-catalyzed) dehydration of the intermediate product to produce cyclohexanone.<sup>26</sup> The afterwards reaction pathway are similar to that of phenol, that is the cyclohexanone convert into bicyclohexyl through aldol condensation.

#### C) Diphenyl ether (4-O-5)

The results of diphenyl ether are similar to the results of phenol, since it decomposes to phenol and benzene through C-O

cleavage. Significant amounts of recombination dimeric compounds, bicyclohexane, were also observed as well. The effect of noble metals, cations and anions of ILs are also similar to the results of phenol. It is declared that the cleavage of C-O can take place via either the acid-catalyzed hydrolysis or NPs-catalyzed hydrogenolysis.<sup>64</sup> However, the conversion of diphenyl ether was failed without phosphoric acid under 5 MPa  $H_2$  at 130 °C for 10 h. So the only route at this reaction conditions is that diphenyl ether is firstly hydrolyzed to phenol and benzene through the acid site. Then the afterward steps are the same as the HDO of phenol, so the products distribution of diphenyl ether are the same with phenol. The only difference between phenol and diphenyl ether is the good performance of Pd NPs, and this phenomena owning to the easier hydrogenation of benzene than phenol.



Scheme 3 Reaction pathway of guaiacol in the catalytic hydrogenation treatment



Scheme 4 Reaction pathway of diphenyl ether in the catalytic hydrogenation treatment





Figure 8 Yield of products from HDO of guaiacol over the Pd, Pt, Ru, Rh NPs prepared in [Bmim]PF<sub>6</sub> and the result in Reference (Left); Yield of different ILs over Pt (Right) (T: 130 °C, P: 5 MPa,10 h; H<sub>3</sub>PO<sub>4</sub> 0.1 g, [Bmim]PF<sub>6</sub> 2g, Substrates/Pt=100)

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DOI: 10.1039/C5GC03121D Journal Name

 D) 2-phenylethyl phenyl ether (β-O-4), Benzyl phenyl ether (α-O-4) and Benzofuran (β-5)



(II) Benzyl phenyl ether  $\sqrt[4]{0^{\alpha}}$   $\sqrt[NPs/IL, H_3PO_4]$  + + +



Figure 9 Yield of products over the Pd, Pt, Ru, Rh NPs prepared in  $[Bmim]PF_6$  and the result in Reference (Left); Yield of different ILs over Pt (Right) (T: 130 °C, P: 5 MPa,10 h; H<sub>3</sub>PO<sub>4</sub> 0.1 g, [Bmim]PF<sub>6</sub> 2g, Substrates/Pt=100)

 $\beta$ -O-4 bonds are the most abundant C-O bonds in lignin.<sup>6, 65</sup> The HDO/C-O cleavage performed good to yield the corresponding products, cyclohexane and ethylcyclohexane. However, there are still side reactions to form bipolymer, such as bicyclohexane and 1,2-dicyclohexylethane. Theoretically, one mole 2-phenylethyl phenyl ether would yield one mole cyclohexane and one mole ethylcyclohexane. Actually, the amount of ethylcyclohexane is more than cyclohexane owing to

less activity in the side reactions. Compare with cyclohexanol, the 2-cyclohexylethanol is more inactive when reaction with proton via electrophilic aromatic substitution and aldol condensation, so majority of 2-cyclohexylethanol converts to ethylcyclohexane.

The results of benzyl phenyl ether are similar to the results of 2phenylethyl phenyl ether conversion, and the Pt NPs shows the best yield, while the Ru is the worst one due to the selectivity. The yields of two main products are lower compared to other metals. The highly reactive Ru NPs may be the reason for the appearance of dominant side produce.

The catalytic activity of metal site for benzofuran is very different from others reactants, which decreases with the order of Pd > Rh ~ Pt >> Ru. The [Bmim]PF<sub>6</sub> shows much better performance in selectivity than the ILs with BF<sub>4</sub> or NTf<sub>2</sub> anions.



Figure 10 Comparsion between different ILs and NPs

#### 3.2 The Effect of Metal, Anions and Cations of ILs

Converge all the results in one figure, the region with high conversion and high selectivity is zoomed in to select the best combination of IL and noble metal. The most versatile combination is the  $Pt/[Bmim]PF_6$  which provided full conversion for most model compounds with selectivity higher than 90%.

The catalytic selectivity of metal for HDO/C-O cleavage decreased with the order of  $Pt > Rh \sim Ru >> Pd$  in most cases. The precise method of titrating the number of active sites of NPs hasn't been found yet.<sup>66</sup> In most cases, it is assumed that only the surface atoms of NPs are active in catalytic reaction.<sup>45</sup> Thus the activity and selectivity are only attributed to the size of the NPs and the type of unit cell of metal.

The mean sizes of NPs are estimated through TEM. The poor performance of Pd NPs owing to their large particle sizes even before reaction is clearly shown in Table 2 and Figure 10. The better selectivity of Pt NPs than Rh and Ru NPs are corresponding to the order of mean diameter Pt > Rh > Ru. The smaller NPs with lager effective contact area with reactants are more active in the catalytic reactions, while lead to more side reactions with less selectivity. Comparing with the diameter before the reaction, the slightly increased mean diameters of NPs indicates the possibility of recycling.

Apart from particle size, the surface atom is determined by the type of unit cell as well. The XRD data displays the type of unit cell of NPs in Figure 5. The surface atoms of fcc are more than these of hexagonal in the same size. So Pt and Rh NPs are more active and less selective than Ru NPs when their sizes are the

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same in theory. While the selectivity decreases with the order of  $Pt > Rh \sim Ru$ , so it is concluded that the activity and selectivity are strongly dependent on the particle size rather than the type of unit cell.

Considering the conversion depends on the nature of the IL as well, a series of anions or cations are used in the conversion of model compounds. A small decrease in selectivity is caused by the increase in the length of alkyl chain of the cations. When the length of the alkyl chain is six, the yield of main product decreased obviously. The degree of organization in imidazolium based ILs strongly depends on the presence of a hydrogen atom at the C2 position of the imidazolium ring.<sup>67, 68</sup> With longer alkyl chain, the structure of ILs tends to have more aggregations in microscale.<sup>67, 69-71</sup> This non-uniform and co-adjacent structure leads to the formation of instable NPs which caused NPs agglomeration. Furthermore, a recent study has state that the longer alkyl chain of cations resulted in smaller NPs size.<sup>72, 73</sup> Thus the shorter the alkyl chain leads to higher the selectivity.

However, the anions of ILs have great impact on the reaction. ILs with NTf2 and PF6 anions are found to be more effective than ILs with BF4 due to their different hydrophobic properties. The hydrophilia of ILs may affect the reaction, since the NPs are sensitive to water. The small amount of water may cause the aggregation of NPs which would result in the deactivation of catalysts. The gas solubility also strongly depends on the nature of the anion while it has only a minor relation with the cation.<sup>74</sup>, <sup>75</sup> It is believed that the higher gas solubility would contribute to the hydrogenation. Since more hydrogen dissolved in ILs than in water or most solvents, the possibility of the contact between hydrogen and the surface of NPs would increase and the activation of hydrogen by the NPs could also be easier. The solubility of hydrogen in various ILs with different anions are decreased with the following order: [Bmim]NTf<sub>2</sub> > [Bmim]PF<sub>6</sub> >  $[Bmim]BF_4 > H_2O.^{76-79}$  In addition, the NPs size increases with the size of the anions.<sup>80</sup> The polar precursors are preferentially dissolved in polar domains, then the reduction and NPs growth occurs in the polar domains as well.<sup>81</sup> Since the volume of the polar domains are controlled by the size of anions, the NPs size decreases linearly with the molecular volume of the anion in the order of  $[Bmim]BF_4 > [Bmim]PF_6 > [Bmim]NTf_2$ . As a result, the order of selectivity is  $[Bmim]BF_4 > [Bmim]PF_6 >$ [Bmim]NTf<sub>2</sub>, which is the same with the experiment results except the [Bmim]BF4. The reason of low conversion in [Bmim]BF<sub>4</sub> may be caused by the large NPs size, which is inactivate in the hydrogenation.

#### 3.3 Conversion of Dealkalized Lignin and Organosolv Lignin

Using the best combination of Pt and [Bmim]PF<sub>6</sub> for dealkalized lignin and organosolv lignin reactions at the same conditions as previous, the liquid products yield is only 5% and 3%, respectively. The selectivity of main product cyclohexane is accounting for 68% and 49%, respectively. In the reductive depolymerisation step, C-O bonds in lignin with aromatic network polymer chains are more inactive than these in model compounds. The depolymerisation of dealkalized lignin and



DOI: 10.1039/C5GC03121D

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Figure 11 The effect of the amount and types of acid (T: 130 °C, P: 5 MPa, 10 h; [Bmim]PF<sub>6</sub> 2g; Diphenyl ether /Pt=100)

organosolv lignin are more difficult to occur than the lignin model compounds.

During the depolymerisation, self-condensation reactions of the lignin fragmentation are forming new C-C bonds that may be counteracting depolymerisation.<sup>82</sup> In addition the crosslinking reactions are more prone to occur under acid conditions or in the presence of radicals.<sup>83</sup> Nevertheless, it was unusually to find products at such low temperature.<sup>84</sup>

#### 3.4 The Effect of Acid

In Figure 11, the conversion of diphenyl ether increases with the amount of acid at first, after the amount of acid is up to 0.1 g, the conversion is kept at 100%. The selectivity hardly changed with the acid amount. One of the drawbacks of this catalyst system is the un-avoided side reactions, and the potential environmental damage by the dispose of phosphoric acid even though it can be recycled. It is recommended to use solid acids to replace it. A parallel experiment is carried out at the same condition to use Amberlyst 15(H) as the catalyst instead of  $H_3PO_4$ . The trend of conversion and selectivity are similar to  $H_3PO_4$ . At the same dosage, the conversion of solid acid is lower than  $H_3PO_4$ . The slight lower activity of solid acid may be caused by the limited mass transfer. Nevertheless solid acid is still promising in this system.

#### 3.5 The Recycling Test

The slightly increased in diameter after reaction indicates the possibility of reusing the catalyst. After three times recycling, the  $Pt/[Bmim]PF_6$  still can full converts the substrate without losing any activity. The inactivation of catalyst may be caused by the increase of the size of the NPs after each reaction. The lost of NPs at each run may another main reason as well.



Figure 12 Catalyst recycles of diphenyl ether (T: 130 °C, P: 5 MPa, 10 h; [Bmim]PF<sub>6</sub> 2g; Diphenyl ether /Pt=100)

#### Conclusions

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Pt/[Bmim]PF<sub>6</sub> is an effective pseudo-homogeneous catalytic system for the C-O cleavage and HDO of lignin model compounds. This catalytic system is capable of fully conversion of lignin model compounds at mild temperature with high selectivity. The catalytic selectivity of metal for phenol hydrodeoxygenation to cyclohexane and C-O cleavage of diphenyl ether was found to follow the order of  $Pt > Rh \sim Ru >>$ Pd. The difference in the selectivity may mainly ascribe to the particle size as proven by TEM. The length of the alkyl chain in cation has slight impact on the selectivity, while the hydrophilic [Bmim]BF<sub>4</sub> could hardly convert the model compounds. The recycling test is the evidence of the well robustness of the catalyst which do not lose activity for at least 3 runs. The conversions of dealkalized lignin and organosolv lignin showed the potential of this pseudo-homogeneous catalyst for offering a practical process options for the production of cyclohexane from lignin even though the conversion is quite low. Nevertheless, a meaningful advantage of this process is that the main product cyclohexane accounts over 50% in the product stream. Although these results are encouraging, future technical development needs focus on the ability of catalysts to tolerate high temperature.

#### Acknowledgements

This work was supported by International S&T Cooperation Program of China (2014DFA61670), National Natural Science Foundation of China (No. 21210006, 21576269, 21276260, 21406230) and External Cooperation Program of BIC, Chinese Academy of Sciences (No. GJHZ201306).

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