New insights into the catalytic cleavage of the lignin \( \beta-O-4 \) linkage in multifunctional ionic liquid media†

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Ionic liquids are attractive reaction media for the solubilisation and depolymerisation of lignin into value-added products. However, mechanistic insight related to the cleavage of specific linkages relevant to efficient lignin depolymerisation in such solvents is still lacking. This study presents important insight into the scission of the most abundant lignin \( \beta-O-4 \) motif in Brønsted acidic ionic liquids. Using relevant model compounds, cleavage products were identified and undesired side reactions examined carefully. Stabilisation of reactive intermediates was achieved in ionic liquids comprising both Brønsted acidic function and stabilized nanoparticles that comprise hydrogenation activity in order to suppress undesired side reactions. Especially, the in situ hydrogenation of the aldehyde intermediate originating from the acid-catalysed cleavage of lignin beta-O-4 model compounds into more stable alcohols was investigated. This is the first time that such products have been systematically targeted in these multifunctional reaction media in relation to lignin depolymerization.

Introduction

Before the widespread use of fossil carbon sources at the beginning of the 20th century, carbon-based compounds such as terpenes, methanol, and acetone were derived from wood.1 Due to the finite nature of fossil carbon resources, the focus has shifted again to the use of renewables.2 Utilization of lignocellulosic biomass for the chemical industry ideally requires valorisation of all its components.2a,3 Lignin, a major component of lignocellulosic biomass (15–35 wt%), could serve as a renewable source of aromatic bulk and fine chemicals.3a,4 However, depolymerization of lignin to aromatic monomers has thus far proven to be challenging due to its amorphous and recalcitrant nature.5 In lignin, aromatic monomers are randomly cross-linked via C–C and C–O bonds (Fig. 1).5 The most abundant linkage is the \( \beta-O-4 \) alkyl–aryl ether.5a,5b Effective cleavage of this bond is seen as the key strategy for low-temperature depolymerisation of lignin into desirable monomeric aromatic compounds in relatively high yields.4c,7 To this end, new strategies have been developed using representative \( \beta-O-4 \) model compounds, for which results are summarized in recent reviews.3b,4,5b,7,9c In particular, several studies have recently highlighted the need for stabilization of reactive cleavage products in order to suppress recondensation reactions that lead to decreased monomer yields.8

Ionic liquids (ILs) have many desirable characteristics for use as green reaction media, such as negligible vapour pressure, chemical inertness, tuneable polarity, acidity, basicity and tuneable miscibility with other solvents.9 Moreover, ILs have been reported as excellent solvents for the notoriously hard-to-dissolve lignin fractions10 and have shown great potential for the fractionation of lignocellulose components.9c,11 Therefore, the development of lignin depolymerisation methodologies in ILs is very attractive.

One particularly intriguing field is the synthesis of nanoscale metal catalysts of controlled size and shape, namely metal(0) nanoparticles (M-NPs).12 M-NPs stabilized in ILs have been shown by us and others to possess a variety of attractive properties for use in catalysis13 and have found several interesting synthetic applications recently.14 A recent development showed that ionic liquids may act in particular cases not only as solvent, stabilizing and protecting agents for the formed nanoparticles, but selected ions also suitably act as very mild reducing agents.13b,c,15

† Equal contribution.

‡ CrossMark

Received 14th September 2015, Accepted 16th October 2015
DOI: 10.1039/c5cy01554e
www.rsc.org/catalysis

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[BMIM][OAc]$_3$) are capable of acting as mild reducing agents. The advantage of this approach is that external reducing agents as additives such as hydrogen, hydrazine or metal borohydrides are unnecessary. Moreover, the reducing process is slower than that in the presence of hydrogen which implies that the local metal(0) concentration is kept low, avoiding fast particle growth leading to undesired large particles but allowing the synthesis of small particles. The nanoparticle catalysts can be directly used for application in catalysis, such as hydrogenation of arenes$^{13b,15c}$ (partial) hydrogenation of C–C$^{12a}$ as well as carbon–hetero multiple bonds,$^{15c,16}$ C–C bond cleavage$^{13b}$ and C–N coupling reactions.$^{14b,16}$ The incorporation of functional groups into the IL moiety allows the modification of the metal surface with ligands, thus controlling the (chemo)selectivity, for example in hydrogenation reactions.$^{15a-c,16,17}$ In particular, the control of the (chemo)selectivity via catalyst surface modification is of particular interest also for biomass refinery. Efficient hydrodeoxygenation of phenol to cyclohexane was demonstrated using a combination of metal nanoparticles dispersed in IL and Bronsted ionic liquids.$^{18}$

The key novelty in our approach is to use such a catalytic system for the cleavage of lignin linkages and the subsequent stabilization of reactive intermediates via in situ reduction, provided that aromatic ring hydrogenation is not prevalent. Furthermore, ILs would allow for biphasic reactions and separation of the reaction components (Fig. 2).$^{17}$

Bronsted acids are often used to facilitate fractionation of lignocellulose as this leads to bond scission leading to partial depolymerisation of lignin.$^{11d,19}$ In this context, the Bronsted acidic properties of ILs have also been studied for facilitating depolymerisation of lignin into aromatic subunits.$^{10d,11b,20}$ In order to study lignin acidolysis with Bronsted acid ILs, several groups have employed lignin β-O-4 model compounds.$^{19a,21}$ Effective cleavage of the β-O-4 linkage was found using 1-H-3-methylimidazolium chloride ([HMIM][Cl]) at 150 °C by addition of a small amount of water$^{21a}$ or by employing catalytic amounts of Lewis acidic metal chlorides, such as AlCl$_3$ in combination with 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to presumably form [BMIM][AlCl$_4$].$^{21b}$ Here, up to 80% of one of the cleavage products (guaiacol 3) could be obtained. A separate study found no direct relation between the cleavage activity and the IL acidity.$^{21c}$ The results indicated different prevalent cleavage pathways for coordinating and non-coordinating anions (Scheme 1). In these studies, Hibbert ketones$^{22}$ were suggested to be the secondary products. However, exact structures and quantities were not established. Additionally, the formation of higher molecular weight products was indicated.

Identification and quantification of the secondary reaction products are important because in lignin only one set of products is formed that contains both functional groups from the model compound cleavage reactions (alkyl and phenolic sides). Therefore, significant amounts of products can only be obtained from lignin if “both sides” of the model compound are obtained in reasonably high yield after cleavage.$^6$ The pathways observed in ILs are closely related to the established mechanistic insight into acid-catalysed

![Fig. 1 Lignin structure highlighting the β-O-4 linkage and model compounds representing this motif.](image1)

![Fig. 2 Concept of lignin depolymerisation in ionic liquid followed by conversion of reactive intermediates using Ru-NPs and H$_2$ and separation of products.](image2)
conversion in mixtures of water and organic solvents.\textsuperscript{22,b,c,23} The main difference is the observation of the apparent stability of the vinyl ethers in ILs.\textsuperscript{21d}

In this work, we aimed to establish further insight into acid-mediated depolymerisation of lignin in multifunctional ILs. Furthermore, \textit{in situ} stabilization of reactive intermediates in these multifunctional reaction media was envisioned in order to obtain stable cleavage products. For this purpose, the cleavage of lignin \(\beta\)-O-4 model compound 1 was studied in detail with Brønsted acidic ILs, IL-H\(^{+1}\) and IL-H\(^{+2}\), as catalysts (Fig. 3). Additionally, homogeneously dispersed metal nanoparticles in IL were prepared and evaluated as a hydrodeoxygenation catalyst to stabilize the acid-catalysed cleavage product 2, thereby forming more stable 4 or potentially 5.\textsuperscript{8a} Ionic liquid 1-butyl-2,3-dimethylimidazolium \(N\_N\)-bis(trifluoromethylsulfonyl)imide ([BM\(_2\)Im]NTf\(_2\), IL1) was selected for its demonstrated ability to stabilize homogeneously dispersed ruthenium nanoparticles, which have been previously shown to be excellent for \textit{in situ} hydrogenation reactions.\textsuperscript{1,1b} This ionic liquid has the added advantage of not containing an acidic imidazolium proton,\textsuperscript{24} which is expected to provide controlled acidity in the reaction medium.

### Results and discussion

**Cleavage of \(\beta\)-O-4 model compounds using IL-H\(^{+}\) in IL1**

The cleavage activity of IL-H\(^{+1}\) was tested on \(\beta\)-O-4 model compound 1 with IL1 as reaction medium (Scheme 2). The reaction conditions were optimized for the yield of guaiacol 3. As expected, no conversion of 1 was detected in the absence of IL-H\(^{+1}\) demonstrating the lack of acidic protons in the IL1 reaction medium. Upon addition of IL-H\(^{+1}\), high substrate conversion was detected. Increasing the temperature led to higher selectivity for 3 at short reaction times, indicating a fast cleavage reaction and slow decomposition of the reaction products (Fig. 4). The reaction appeared fast compared to previously reported systems in 1,4-dioxane\textsuperscript{8a} and water.\textsuperscript{22,b,23,25} The maximum yield of 3 was 42\% upon using 10 mol\% IL-H\(^{+1}\) in IL1 after 1 minute at 140 °C. Application of 2-phenoxy-1-phenylethanol as the substrate provided similar yields of phenol compared to 3.

![Scheme 2](image2.png)

**Scheme 2** Cleavage of \(\beta\)-O-4 model compound 1 with IL-H\(^{+1}\) in IL1.

![Fig. 4](image3.png)

**Fig. 4** Conversion of 1 and yield of 3 in the cleavage of compound 1 (0.1 mmol) with IL-H\(^{+1}\) (0.01 mmol) in IL1 (500 \(\mu\)L) at different reaction times and temperatures.
Unlike in the ionic liquid system employed by Ekerdt et al., we found that the addition of water has no positive effect.\textsuperscript{21}a Our previous work, using triflic acid in 1,4-dioxane, showed excellent yields of \(3\).\textsuperscript{8a} In order to test the potential of biphasic reactions with IL\(1\), mixtures of 1,4-dioxane were tested as reaction medium (Fig. 5). This clearly showed that the addition of 1,4-dioxane has a positive effect. The exact nature of this positive effect is unknown, but this might be related to the stabilization of the reaction products. It should be noted that a 1 : 1 mixture of 1,4-dioxane : IL results in a single phase, while a biphasic system is observed at ratios of 3 : 1 and greater.

A lower substrate concentration was beneficial to obtain higher yields of \(3\) (Fig. 6). This effect has likely to do with the stability of the products in the reaction mixture. The yield of \(3\) could be increased to 61\%, at a substrate concentration of 0.1 \(\text{M}\), at 140 °C and using 5 mol\% IL-H\(1\) (Fig. 7). Increasing the temperature to 160 °C did not improve the yields of \(3\) after 5 minutes. When IL-H\(2\) was used as Brønsted acid, the yields of \(3\) were very similar (around 60\%, Fig. 8). However, in contrast to IL-H\(1\), the application of IL-H\(2\) did lead to slightly improved yields of \(3\) at temperatures above 140 °C. At a reaction time of 5 minutes, over 70\% \(3\) could be obtained at 180 °C and 200 °C. This could be further improved to 74\% \(3\) at 200 °C by decreasing the reaction time to 2 minutes. IL-H\(2\) has less Brønsted acidity compared to IL-H\(1\), and might therefore cause less product decomposition. Overall, the yields of \(3\) following cleavage 1 with IL-H\(2\) at 200 °C at low reaction times are an improvement over earlier reported reactions of \(\beta\)-O-4 model compounds in acidic IL or IL media.\textsuperscript{19,21}

Side reactions involving cleavage products
Apart from \(3\), typically complex mixtures of products were observed by HPLC (Fig. 9a). Using IL-H\(2\) at elevated temperature provided much cleaner reaction mixtures as well as less
coloured solutions (Fig. 9b). Identification by LC-MS analysis revealed the dehydration product 6 as a mixture of \(E\) - and \(Z\) -isomers, which were previously reported as major products starting from \(\beta\)-O-4 model compounds in ionic liquid media.\(^\text{21c,d}\) The observation of 6 reveals that, although substrate conversion is high, not all of the dimers are in fact cleaved, even at high temperatures. This is likely caused by the stabilization of carbocation intermediates obtained upon dehydration in the ionic medium.\(^\text{10c,19a,26}\) Although this explains why selectivity towards 3 never reaches 100%, it does not provide evidence on the fate of the second cleavage product that consequently has to be formed upon release of 3. Column chromatography allowed for isolation of 2-phenylnaphthalene 7 from the reaction mixture. Formation of 7 was confirmed using an authentic sample, which also allowed for quantification. Formation of up to 10% was found in reactions that gave relatively high amounts of 3 at high reaction temperature and time. Up to 20% of 7 could be obtained at prolonged reaction times (1 hour). Additionally, when HOTf or MeSO₃H were applied as Brønsted acid in IL1, relatively high amounts of 7 were observed (up to 20%). 7 originates from acid-mediated aldol condensation of aldehyde 2 and the subsequent condensation and dehydration (Scheme 3).\(^\text{27}\) These results highlight the dehydration potential of these catalytic systems. Other signals found by HPLC may be related to other products originating from aldol condensation reactions or other condensation reactions of 2 (e.g. condensation of 3 and 2, which would be in line with the observation of the decomposition of 3). Furthermore, side products can originate from the condensation reaction between the carbocation intermediate and the aromatics in the product mixture. Products related to 7 obtained from lignin would be functionalized (phenolic) polycyclic aromatic compounds. Tuning the properties of the IL system to prefer such pathways for the formation of polycyclic aromatics from lignin is an interesting future direction to explore.

Trapping the aldehyde cleavage product with ethylene glycol

Recently, we reported on a novel methodology to increase the yields of the cleavage products by trapping the aldehyde 2 with ethylene glycol to obtain the corresponding acetal 8.\(^\text{8a}\) Moderate yields of 8 were also obtained upon the addition of ethylene glycol to the cleavage reaction of 1 in IL1 using IL-H⁺1 as a catalyst (Scheme 4, Fig. 10). In line with the results presented above, lower catalyst loadings led to higher yields of products 8 and 3. Increased reaction times resulted in significantly lower yields. From these observations it can be concluded that 8 is not a stable product in this reaction medium. A similar degradation of 8 was previously observed in toluene at the same temperature with triflic acid as the Bronsted acid catalyst.\(^\text{10a}\) Using triflic acid in the ionic liquid medium led to very low yields of

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**Fig. 9** Representative HPLC chromatograms showing identified signals of a) 140 °C, 30 min, 0.1 mmol of 1, 0.2 M in IL1, 10 mol% IL-H⁺1; b) 200 °C, 2 min, 0.05 mmol of 1, 0.1 M in IL1, 5 mol% IL-H⁺2.
Formation of 7 was observed in the reaction using ethylene glycol. Additionally, an increased yield of 3 was detected. These observations indicate that another decomposition pathway for 2 could be Friedel–Crafts hydroxalkylation of 3. These results highlight the need for direct conversion of reactive aldehydes formed upon cleavage of the lignin β-O-4 linkage.

Synthesis and characterization of ruthenium nanoparticles

Ruthenium nanoparticles were employed to stabilize the reaction products by in situ hydrogenation of the reactive aldehyde product to the corresponding alcohol. For this purpose, ruthenium nanoparticles were dispersed in IL1 according to a literature procedure developed for similar ionic liquids by heating of a Ru(cod)(methylallyl)₂ solution. The formation of homogeneously dispersed ruthenium nanoparticles (Ru-NP@IL1) was confirmed by TEM measurements, and the size distribution was determined, showing an average size of 3.0 ± 0.3 nm (Fig. 11). These results are comparable to nanoparticles homogeneously dispersed in related ionic liquids.

Cleavage in bifunctional ionic liquid reaction media

Cleavage of 1 combined with in situ hydrogenation of the reactive aldehyde intermediate to 2 was performed using Ru-NP@IL1 as the hydrogenation catalyst (Scheme 5). Several products were anticipated through sequential dehydration and hydrogenation steps based on earlier experience with in situ hydrogenation reactions following the acid-mediated cleavage of 1. Initial experiments were performed overnight using IL-H⁺ as the Brønsted acid catalyst in IL1. Low IL-H⁺ loading (≤1 mol%) resulted in high conversion of 1. However, the main products corresponded to 1 in which the β-O-4 ether was not cleaved and the aromatic rings were hydrogenated. Additionally, small amounts of aromatic monomeric products that were formed were completely “over-reduced” to the corresponding cyclohexane compounds. Increasing the amount of IL-H⁺ gave moderate yields of 9 at reaction times from 1 to 4 hours (Fig. 12a). Surprisingly, at these high loadings, incomplete conversion was observed after 1 hour. Increasing the reaction time resulted in full conversion and a small increase in the yields of 3 and 9. Lowering the amount of IL-H⁺ did not lead to improved yields of 3 and 9. These experiments indicate that the addition of the Ru-NP@IL1 lowers the overall rate of the cleavage of 1, which is greater in IL-H⁺ alone; thus the two catalysts affect each other. In conjunction with the ethylene glycol trapping experiments, the application of a stabilization strategy that converts the reactive aldehyde 2 in situ leads to near equimolar yields of the two cleavage products. Small amounts (up to 15%) of 11 and ring hydrogenation products of 11 and 1 were also detected as side products. Saturated compound 11 is the result of
sequential dehydration and hydrogenation of 1 and was previously found to be resistant to acid-catalysed cleavage. Additionally, hydrogenated monomeric compounds 9h and 10h were observed as minor products (<3%) as well as small amounts (<1%) of further dehydration and hydrogenation of 9 to 10. This stands in contrast to earlier reports from comparable reactions in 1,4-dioxane with triflic acid and 5% Ru/C, where 10 was a major product.

Consistent with the cleavage reaction of 1 with IL-H⁺1, the yields of 3 could be increased to over 60% upon application of a mixture of IL1 with 1,4-dioxane (Fig. 12b). Under these conditions, moderate yields of 9 were obtained even at lower ruthenium loading, while similar amounts of non-cleaved dimers were observed. At lower concentrations of IL-H⁺1, significant amounts of 2 were found in the mixture. This is in contrast to the reaction without 1,4-dioxane where only traces of 2 (<2%) were detected. The observed amounts of 2 are counter-intuitive, yet remarkable, as 2 is typically unstable under acidic conditions. This could be caused by several factors. For example, 2 might be separated from the acidic IL layer by solvation in the 1,4-dioxane layer. Additional measurements with authentic standards in a 1,4-dioxane:IL (4:1) biphasic mixture confirmed the preference of 2-phenylacetaldehyde for the 1,4-dioxane layer (see the ESI† section 4). This likely plays a role in temporary separation of the aldehyde from the acidic IL layer and allows for more controlled hydrogenation to take place, without extensive recondensation due to the build-up of the aldehyde in the IL phase. Additionally, 1,4-dioxane might effectively reduce the acid strength of the reaction medium leading to the suppression of side reactions.

Brønsted acid catalyst IL-H⁺2 was also assessed for the cleavage of 1 in combination with Ru-NP@IL1 (Fig. 13). In this case, with 20 mol% IL-H⁺2, no significant amounts of 9 and 3 were found. Significant amounts of 11 and hydrogenated substrates were detected instead. By increasing the amount of IL-H⁺2 to 40 mol%, cleavage products of 1 were observed as well as residual 2. Further increasing the amount of IL-H⁺2 led to additional formation of 9 and 3. Again, yields of 3 and 9 could be increased by the addition of 1,4-dioxane. Up to 53% 9 was obtained. The cleavage of 1 with IL-H⁺2 showed optimal cleavage product formation at temperatures above 140 °C. Therefore, in situ hydrogenation was performed at 180 °C. Repetitively, the cleavage activity of the bifunctional catalytic system was surprisingly low compared to the cleavage reactions without Ru-NP@IL1. Complete substrate conversion was obtained after 5 minutes at 180 °C, while in the presence of Ru-NP@IL1, after 1 hour the reaction was still incomplete (compare Fig. 8 and 14 entries for 180 °C).

Fig. 12 Conversion of 1 and yields of 2, 3 and 9 in the cleavage of compound 1 (0.1 mmol, 0.2 M) in a) IL1 and b) 60% 1,4-dioxane in IL1 at 140 °C with IL-H⁺1, 40 bar H₂, Ru-NPs@IL1 (30 mol% [Ru] (a) and 7.5 mol% [Ru] (b)).

Fig. 13 Conversion of 1 and yields of 2, 3 and 9 in the cleavage of compound 1 (0.05 mmol) in IL1 with IL-H⁺2 and Ru-NPs@IL1 (30 mol% [Ru]).

Fig. 14 Conversion of 1 and yields of 2, 3 and 9 in the cleavage of compound 1 (0.05 mmol, 0.1 M) in IL1 with IL-H⁺2 and Ru-NPs@IL1 using 180 °C temperature bursts at 10 bar H₂.
Leaving the reaction for 2 hours led to full conversion of 1 and increased amounts of 3 and 9 showing a progressive reaction. In these experiments, significant amounts (up to 15%) of 10 was observed, revealing the positive effect of the temperature on the subsequent dehydration/hydrogenation of 9.

The above results indicate that harsher reaction conditions (temperature and acid strength) are required for effective cleavage of 1 with IL-H+2 in the presence of Ru-NP@IL1. The hydrogenation activity of Ru-NP@IL1 was relatively low under these conditions. However, extended reaction times at temperatures of 140 °C or higher seemed to increase ring hydrogenation as well as other undesired side reactions. To overcome this, relatively short temperature bursts at 180 °C were applied followed by further reaction at lower temperature to allow for consecutive hydrogenation of any remaining 2 (Fig. 14). Similar yields of 3 were obtained when compared to a reaction at 180 °C for two hours, indicating a fast cleavage reaction. As anticipated, the short temperature burst following a subsequent reaction at 100 °C did not lead to improved yields of 9 (up to 64%). This supports the hypothesis that cleavage is relatively fast and hydrogenation is relatively slow. Additionally, under these conditions, less side products were observed that arise from ring hydrogenation of the substrate as well as 11. Despite using the “temperature burst” method, the Bronsted acidity and the loading of the hydrogenation catalyst could not be reduced.

The fate of the ruthenium nanoparticles

In order to better understand the low hydrogenation activity under reaction conditions, the hydrogenation of 2 alone by Ru-NP@IL1 was studied. The nanoparticles performed well in the reported hydrogenation reactions (Table S1†). Additionally, hydrodeoxygenation of phenol and cyclohexanol was successful in the presence of IL-H+1 although with lower activity (Table S2†). In most of the reactions using 1 as the substrate, agglomeration of the ruthenium nanoparticles was observed. This effect was not observed by solely heating the Ru-NP@IL1 to high temperatures. However, when the same experiment was repeated in the presence of the substrate, significant agglomeration was observed. This indicated a possible deactivation of the ruthenium nanoparticles, which could not be recycled in these reactions. Hydrogenation of 2 by Ru-NP@IL1 in the absence and presence of IL-H+2 was followed in time (Fig. 15). In the absence of Bronsted acid, 2 was initially converted to 9; however hydrogenation activity significantly decreased over time to stall at a maximum 41% yield of 9 after 3 hours. In the presence of IL-H+2, 2 was quickly converted. However, selectivity to 9 was low, reaching a maximum of 32% after 30 minutes. The initial rate was higher with 24% of 9 formed in the first 10 minutes compared to 6% of 9 in the absence of IL-H+2. Thus, the Bronsted acid catalyst appears to have a positive influence on the hydrogenation activity, an effect that has been previously observed for ruthenium hydrogenation catalysts.29 This explains that when short- and high-temperature bursts were applied, the best results for the yield of 9 were obtained. Under these conditions, 1 rapidly cleaved and produced 2 rapidly hydrogenated to 9 before the catalyst lost its activity.

Conclusions

This study demonstrates that the stabilization of the reactive intermediates formed upon acid-catalysed cleavage of lignin model compounds in ionic liquids is a desirable strategy. For the first time a proof of principle is provided for the in situ catalytic conversion of these unstable fragments, taking advantage of the modular, multifunctional nature of this alternative reaction medium.

The acid-catalysed cleavage of β-O-4 lignin model compound 1, using Bronsted acidic IL media, confirmed earlier observations that good selectivity to guaiacol 3 can be achieved.21 Isolation of 2-phenylnaphthalene 7 from the reaction mixture revealed 2-phenylacetalddehyde 2 as the secondary cleavage product in agreement with studies in conventional reaction media.8a,22b,23,25 Further efforts focused on the stabilization of 2 in situ to obtain acetals or alcohols. By addition of ethylene glycol, 2 was converted to 2-benzyl-1,3-dioxolane 8 in equimolar amounts to 3. By employing bifunctional reaction media containing both a Bronsted acid catalyst and Ru-NP@IL1 as the hydrogenation catalyst, good yields of 2-phenylalcohol 9 could be obtained. This is the first time good combined yields of monomeric products were obtained from reactions in ionic liquids.

When these results are related to the selective depolymerization of lignin as an aromatic polymer with predominantly β-O-4 linkages, phenolic products are obtained that are a combination of 2 and 3. Therefore, good selectivity for both types of products is essential for the successful application of such methodology on lignin. Thus, the present study explains
the low monomer yields in early attempts of lignin depolymerisation in ionic liquid media\textsuperscript{10,11,19} which in model compounds only provided good yields of one cleavage product.\textsuperscript{19a,21a}

Future studies should focus on improving the stability of these catalytic systems in order to prevent agglomeration of the metal nanoparticles in the presence of the substrate. Additionally, aromatic ring hydrogenation activity should be minimized. Further tailoring the acidity of the reaction medium, and the nature of the nanoparticles, for example copper-based NP@IL, should lead to improved catalytic systems for effective dissolution and depolymerisation of lignin. This could be combined with efficient product separation in an IL/organic biphasic system.

Acknowledgements

M. Scott is thankful for a scholarship from the Evonik Foundation. P. J. Deuss, J. G. de Vries and K. Barta gratefully acknowledge financial support from the European Commission (SuBiCat Initial Training Network, Call FP7-PEOPLE-2013-ITN, grant no. 607044). M. H. G. Prechtl gratefully acknowledges the financial support provided by the Ministerium für Innovation, Wissenschaft und Forschung (NRW-Returnee Award 2009), the Deutsche Forschungsgemeinschaft (Heisenberg-Program), and the Ernst-Haage-Foundation (Max-Planck Society).

Notes and references


