Nanoparticle Catalysis

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Hydrodeoxygenation of Lignin-Derived Phenols into Alkanes by Using Nanoparticle Catalysts Combined with Brønsted Acidic Ionic Liquids[**]

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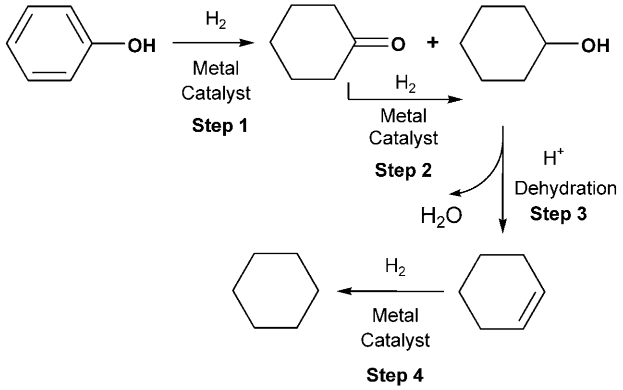
Lignin is a promising feedstock for the production of biofuels due to its availability (15–30 wt % of wood-based biomass) and markedly lower oxygen content than polysaccharides.[1] Considerably more efforts have been paid to the conversion of polysaccharides;[2] nevertheless, the development of lignin-based biofuels is attracting increased attention. Current strategies to produce biofuel from lignin are typically based on two-step processes, in which lignin is first depolymerized into a mixture of simple aromatic compounds (mostly phenols) either by hydrogenation,[3] alkaline[4] or acid[5] hydrolysis, or fast pyrolysis,[6] which is then followed by upgrading into fuels, preferably by hydrodeoxygenation into alkanes. Many advances have been made in the degradation of lignin into phenols; for example, phenolic fractions can be readily obtained by fast pyrolysis from pure lignin[3c,d,6a] or directly from wood biomass,[6b–e] the latter now being a commercialized process.[7] The second step, that is, the transformation of phenolic compounds into hydrocarbon fuels or other chemicals remains a challenge.[8] The conventional hydrodeoxygenation process based on NiMo and CoMo sulfite catalysts is potentially problematic due to sulfur contamination, coke accumulation, and water-induced catalyst deactivation.[9] Recently, aqueous-phase catalytic systems that convert phenolic compounds into alkanes in a series of hydrogenation and dehydration reactions have been reported (Scheme 1),[10,3e] which overcome the problems encountered with conventional catalytic systems. While the new system is ideally suited for lignin-based phenolic substrates, it contains several intrinsic limitations—the most obvious is that a dehydration reaction takes place in water. In fact, a previous case study on the dehydration reaction of cyclohexanol to cyclohexene showed that at 100 °C the equilibrium is > 50 % cyclohexanol in water and decreases dramatically to 2 % when the water content in the system is reduced to 10 %.[11] Consequently, high reaction temperatures exceeding 250 °C are required in aqueous systems, which not only implies demanding process engineering, but also high energy consumption.



Scheme 1. Key steps involved in the formation of cyclohexane from phenol, a lignin-derived model compound used as an example.

The use of ionic liquids (ILs) could, in principle, overcome these problems as well as maintain the advantages of a water-based system (high efficiency, phase separation, etc.). Indeed, ILs have been shown to be promising solvents in biofuel production, especially in the transformation of cellulose[12] and in the production of biodiesel.[13] Nevertheless, examples of lignin-based fuel production in ILs remain scarce.[14] Here, we describe the development of a bifunctional catalytic system based on metal nanoparticles (NPs) and ILs, which can effectively convert lignin-derived phenols into alkanes under mild conditions.

As can be seen in Scheme 1, the reaction pathway includes catalyzed hydrogenations and a dehydration step that is catalyzed by a Brønsted acid. Following Dupont's pioneering work,[15] many notable examples of hydrogenation reactions using nanocatalysts dispersed in ILs have been reported.[16] Indeed, we have developed a series of NP catalysts that are highly efficient for the hydrogenation of C=C,[17] C=O,[18] and aromatic compounds[19] in ILs under mild conditions. However, to the best of our knowledge, the dehydration reaction shown in Scheme 1 has not been achieved in ILs, although many other reactions catalyzed by acidic ILs are known.[20] Consequently, we thought it would be interesting to use Brønsted acidic ILs to catalyze the dehydration reaction shown in Scheme 1 and then include soluble metal NPs to afford a system capable of converting phenol into cyclohexane in a one-pot process.

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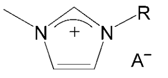
The transformation of cyclohexanol into cyclohexene was selected as a model reaction to evaluate the dehydration reaction in various ILs. The application of classic mineral acids with ILs was not successful: in [bmim][BF_4], H_2SO_4 resulted in the formation of a tar and H_3PO_4 reacted to form an ester with cyclohexanol. Consequently, Brønsted acidic ILs were evaluated.[21] A series of Brønsted acidic ILs, with a SO_3H group covalently linked through an alkyl chain to the cation, were prepared including those with acid-derived anions (**1**–**12** in Scheme 2). The Hammett acidity functions (H_0) of the cations were determined spectrophotometrically,[22] by evaluating the protonation of an uncharged indicator (various anilines, termed I) in acetonitrile, in terms of the measurable ratio of [I]/[IH$^+$]. Representative UV/Vis spectra are provided in Figure 1, in which the unprotonated form of the dye shows an absorbance maximum in the selected range. Essentially, the lower the absorbance maximum in the presence of the acid, the greater the dissociation constant of the acidic IL. Thus, from Figure 1 (top) the acidity of the ILs decreases in the following order, **1** > **2** > **5** > **6** (see the Supporting Information for further details). The Hammett functions of ILs **1**–**12** are compiled in Table S1 in the Supporting Information. The relative acidity of the SO_3H-functionalized ILs (**1**–**7**) is stronger than that of the anion-functionalized ILs (**8** and **9**). Moreover, the acidity of **1**–**7** depends on the nature of the anion, with the triflate salt being the most acidic. ILs **1**–**9** were evaluated as catalysts in the dehydration reaction of cyclohexanol into cyclohexene in [bmim][BF_4] with a good correlation between the strength of the acid and the yield of cyclohexene observed (Figure 2). The strongest acid **1** gave the highest yield of cyclohexene, whereas considerably lower conversions were achieved using ILs **4** and **7**–**9**, which are the weakest acids. Exceptionally, **6** resulted in the second best yield of cyclohexene, probably due to the dehydration power and the poor nucleophilicity of the HSO_4^- ion. It is noteworthy that under the same conditions, but in the presence of water, both **1** and H_3PO_4 afford cyclohexene in low yield, confirming that the IL system is superior to aqueous-based systems for the dehydration reaction.



1: R = $(CH_2)_4SO_3H$, A = CF_3SO_3
2: R = $(CH_2)_4SO_3H$, A = BF_4
3: R = $(CH_2)_4SO_3H$, A = CF_3COO
4: R = $(CH_2)_4SO_3H$, A = CH_3SO_3
5: R = $(CH_2)_4SO_3H$, A = Tf_2N
6: R = $(CH_2)_4SO_3H$, A = HSO_4
7: R= $(CH_2)_4SO_3H$, A = H_2PO_4
8: R = H, A = HSO_4
9: R = H, A = H_2PO_4
10: R = CH_2SO_3H, A = CF_3SO_3
11: R = $(CH_2)_2SO_3H$, A = CF_3SO_3
12: R = $(CH_2)_3SO_3H$, A = CF_3SO_3

Scheme 2. Brønsted acidic ILs used in this study.

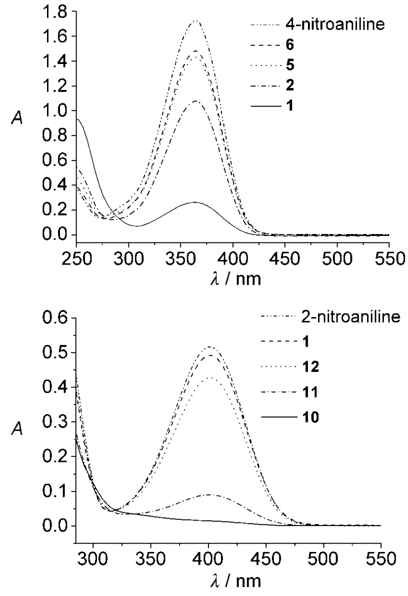


Figure 1. Absorption spectra of 4-nitroaniline (top) and 2-nitroaniline (bottom) for selected Brønsted acidic ILs in acetonitrile.

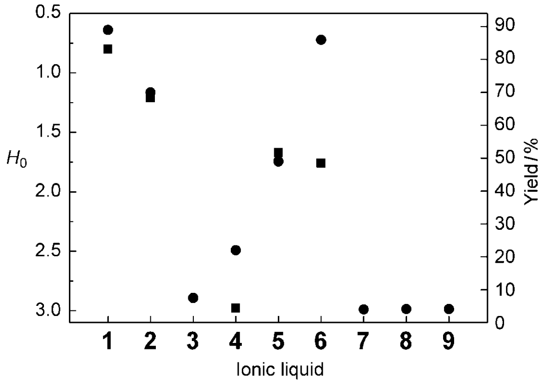


Figure 2. Relationship between acidity H_0 (■) and yield (●) of cyclohexene (for **3**, **7**, **8**, and **9** H_0 was greater than 3.0). Conditions for the conversion of cyclohexanol to cyclohexene: [bmim][BF_4] (1 mL), Brønsted acidic IL catalyst (0.4 M), cyclohexanol (0.1 g, 1 mmol), temperature 130 °C, reaction time 2 h.

Based on these findings the acidity of the ILs was increased through the synthesis of cations with shorter alkyl chains connecting the SO_3H group to the electron-withdrawing imidazolium cation (ILs **10**–**12**, Figure 2). The three new ILs, together with **1**, were tested as catalysts for cyclohexanol dehydration at lower temperatures in both [bmim][BF_4] and [bmim][TF_2N], and as anticipated, ILs **10**–**12** are more efficient than IL **1**, with **10** being the most effective (Table 1). A crystal structure of the 1-methyl-3-methanesulfonate imidazolium zwitterion derived from **10** has been obtained (Figure 3). Notably, the nitrogen–carbon bond (N1–C5) is significantly shorter [1.454(2) Å] than in the 1-butyl-3-butanesulfonate imidazolium system [1.473(3) Å].[23] Other ILs were tested as solvent for the reaction (Table S2, entries 12–15), and [bmim][TF_2N] resulted in highest conversions, probably due to its hydrophobicity allowing the water to be removed from the system once generated.

Table 1: Dehydration of cyclohexanol to cyclohexene under various conditions.[a]

Catalyst	Hammett function	Yield of cyclohexene in [bmim][BF$_4$]	Yield of cyclohexene in [bmim][TF$_2$N]
10	−1.03	94%	96%
11	−0.96	74%	95%
12	0.41	49%	76%
1	0.80	39%	69%

[a] Conditions: solvent (1 mL), Brønsted acidic IL catalyst (0.4 M in solvent), cyclohexanol (0.1 g, 1 mmol), 110 °C, 2 h.

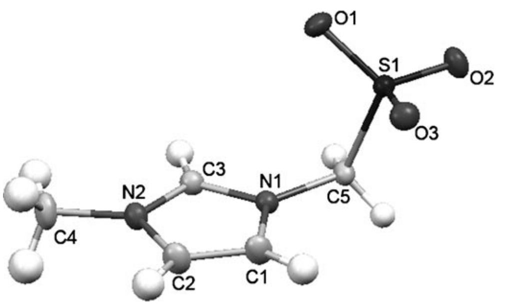


Figure 3. Molecular structure of the 1-methyl-3-methanesulfonate imidazolium zwitterion. Ellipsoids are shown at 50% probability levels. The unlabeled atoms are hydrogen atoms. Selected bond lengths [Å] and angles [°]: N1–C5 1.454(2), S1–C5 1.800(1), N2–C4 1.470(2), S1–O1 1.455(1); N1-C5-S1 110.95(9).

In the next step metal NP catalysts were combined with the Brønsted acidic IL system with the aim of transforming phenols to their corresponding alkanes in a one-pot process. Four different metals were evaluated with Rh NPs prepared directly in ILs and Ru, Pd, and Pt NPs immobilized in the ILs following preparation in water using a literature method.[17] Typically, H_2 was used as the reductant and poly(1-vinyl-3-butylimidazolium chloride-*co*-*N*-vinyl-2-pyrrolidone), an NP stabilizer that is highly soluble in ILs,[18,19] was used as a capping agent. TEM analysis indicated that the size of the Pd NPs was around 5 nm and the size of the other three NPs was smaller, ranging from 2 to 3 nm (Figure 4 and Figure S3 for TEM and HRTEM images). XRD demonstrated the amorphous feature of the Rh, Pt, and Ru NPs (Figure S4). The XRD pattern of the Pd NPs contained several peaks due to their larger size. In the presence of **1** the NP solutions can be stored for months without any signs of degradation.

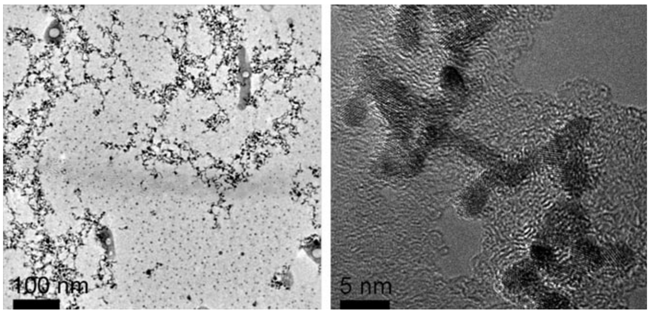


Figure 4. TEM (left) and HRTEM (right) images of the Ru NPs prepared from $RuCl_3$ by H_2 reduction stabilized by poly(1-vinyl-3-butylimidazoliumchloride-*co*-*N*-vinyl-2-pyrrolidone) in water at 130 °C.

The activities of the NP–Brønsted acid–IL systems were evaluated in the conversion of phenol to cyclohexane under hydrogen (40 atm) at 130 °C for 4 h. With the Rh NPs and IL **1** in water the predominant product was cyclohexanol instead of cyclohexane (Table S3, entry 1). Instead, using [bmim][BF$_4$] or [bmim][TF$_2$N] as solvent very high conversions with excellent selectivity to cyclohexane could be obtained. The Pt NPs gave the best selectivity to cyclohexane (98%) at 48% conversion in [bmim][BF$_4$] (Table 2, entry 3) and in [bmim]-[TF$_2$N] the Rh NP containing system resulted in a conversion of 98% with a selectivity to cyclohexane of 84% (Table 2, entry 4). Using the stronger acid IL **10** instead of **1**, the reaction proceeds at 110 °C (Table S3, entries 5 and 6). The Pd NPs were unstable forming metallic precipitates (Table S3, entry 2). whereas the other NPs appear to be stable and can even be recycled. Leaching of the Ru and Rh NPs was not observed (see the Supporting Information).

The bifunctional system may be used to transform a variety of phenolic compounds in both [bmim][BF$_4$] and [bmim][TF$_2$N] (Table 2, entries 5–7 and Table S3, entries 7–14). For the branched phenols only the Rh NP containing system was able to achieve a high alkane yield, suggesting that hydrogenation of the aromatic ring is the limiting factor for the reaction, since Rh is the most active metal in benzene hydrogenation.[24] The combination of Ru and Rh NPs affords a nearly quantitative yield of the alkane product for a challenging substrate (Table 2, entry 8). It is also noteworthy that substrates containing methoxy groups produced methanol.

In conclusion, the transformation of lignin-derived phenolic compounds to alkanes has been achieved in ILs. The catalytic system is composed of metal NPs and a functionalized Brønsted acidic IL immobilized in a nonfunctionalized IL, allowing hydrogenation and dehydration reactions to occur in tandem. Compared to previous systems that are either performed with metal sulfite or with mineral acid/supported metal catalysts in water, this system allows lignin derivatives to be upgraded in an efficient and less energy-demanding process.

Experimental Section

Metal nanoparticles were prepared by H_2 reduction using poly(1-vinyl-3-butylimidazolium chloride-*co*-*N*-vinyl-2-pyrrolidone) as the stabilizer. The hydrodeoxygenation reaction was performed in an autoclave equipped with a heating/cooling system. Detailed synthetic procedures and characterization of the Brønsted acidic ILs and metal nanoparticles, as well as experimental protocol for conversion of phenonlic compounds, are provided in the Supporting Information.

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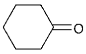
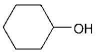
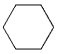
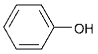
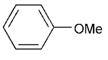
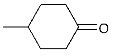
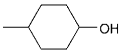
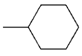
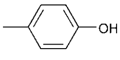
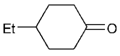
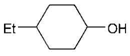
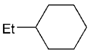
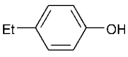
Table 2: Evaluation of the NP–Brønsted acid–IL systems for the conversion of phenols to alkanes.[a]

Entry	Metal	Solvent	Substrate	Conversion	Selectivity			
								MeOH
1	Rh NPs	[bmim][BF$_4$]		95%	23%	10%	67%	–
2	Ru NPs	[bmim][BF$_4$]		77%	0%	3%	97%	–
3	Pt NPs	[bmim][BF$_4$]		48%	0%	2%	98%	–
4	Rh NPs	[bmim][TF$_2$N]		98%	16%	0%	84%	–
5	Rh NPs	[bmim][TF$_2$N]		99%	25%	2%	73%	15%
								
6	Rh NPs	[bmim][TF$_2$N]		98%	14%	0%	86%	–
								
7	Rh NPs	[bmim][TF$_2$N]		99%	16%	0%	84%	–
8	Rh/Ru NPs	[bmim][TF$_2$N]		99%	1%	0%	99%	–

[a] Conditions: solvent (1 mL), substrate (1 mmol), metal/substrate 300:1, **1** (0.2 M in solvent), H$_2$ (40 atm), 130°C, 4 h.

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