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Ionic liquid-stabilized nanoparticles as catalysts for the conversion of biomass

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Biomass resources represent a renewable feedstock of chemicals and fuels to meet the demands of our modern society; however, development of novel catalytic transformations and processes is required to realize a sustainable value chain. Metal nanoparticles stabilized by ionic liquids (NP@ILs) are attractive catalysts for biomass conversions as the overall properties of the catalytic system can be tailored by selecting a suitable combination of the IL and metal nanoparticle components. While the metal nanoparticles define the principle catalytic transformation, the IL provides a stabilization matrix that can tune the surface reactivity of the metal nanoparticles through alteration of the IL cation or anion. Furthermore, the solvation properties of ILs allow the substrate to have direct access to the active sites and effective separation of the product, enabling catalyst recycling or continuous flow operation. Additional functional moieties can also be incorporated into the IL structure, such as Brønsted or Lewis acid sites, to facilitate sequential bond cleavage or formation processes in reaction cascades. The present review outlines the use of colloidal and supported NP@IL catalysts for the catalytic conversion of a variety of biomass substrates, in which the selected examples have been organized into catalyst systems employing non-functionalized and functionalized ILs in order to illustrate the significant potential multifunctional catalysis possesses in the conversion of biomass.

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1. Introduction

The production of chemicals and fuels from renewable resources is a considerable opportunity and challenge for the chemical industry to oppose climate change and replace depleting petroleum resources.^{1–7} Depending on the regional

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multifunctional catalysts towards the conversion of biomass under continuous flow operation employing metal nanoparticles immobilized on supported ionic liquid phases.

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conditions, different types of biomass feedstocks (e.g., triglycerides, lignocellulose, chitin) have been used as viable alternatives to petrochemicals as they can be produced in large quantities and on short enough time scales to be useful for mankind. Utilization of biomass requires the development of effective chemical and biological catalytic pathways to transform bio-based substrates into bulk or fine chemicals and fuels.⁸ The processing of biomass differs greatly from petroleum refining due to the high degree of oxygenated moieties within biomass as compared to the non-functionalized nature of petrochemicals.⁹ Petroleum-derived hydrocarbons require functionalization steps (e.g., hydration, hydroformylation, oxidation) to provide the chemicals needed in our modern society. In contrast, the platform chemicals acquired from biomass must undergo selective removal of oxygenated moieties to provide an entry into the chemical and energetic value chains.^{10,11} Novel catalytic transformations and processes are needed to achieve the selective deoxygenation of biomass towards platform chemicals and their subsequent conversion to provide a diverse range of value-added products for the chemical industry or tailor-made fuel components.^{12,13}

Metal nanoparticles stabilized in ionic liquids (NPs@ILs) are promising catalysts possessing high catalytic activities and selectivities for transformations such as hydrogenation, oxidation and C–C coupling.^{14–16} Within these catalyst systems, an IL plays the dual role of a NP stabilizer and reaction medium.¹⁷ Non-functionalized ILs provide a combination of steric and electronic stabilization through the formation of ionic aggregates (composed of clusters of IL cations and

anions) to form a protective layer around the NPs and prevent particle agglomeration.^{17–19} NPs@ILs possess high catalytic activities resulting from these loosely bound IL aggregates that can be displaced from the metal surface by incoming substrates providing an ideal balance between the NP stability and the catalytic activity.^{17,20,21} Consequently, the molecular structure of the cation and anion of the IL can exhibit a strong effect on the catalytic behaviour of NPs@ILs.

The IL matrix not only provides a stabilization medium for NP@IL systems, but can also solubilize substrates to facilitate their access to the active particle. This is of particular interest in the conversion of biomass as ILs are known to effectively dissolve raw biomass materials (e.g., wood,^{22,23} crustacean shells²⁴), biopolymers (e.g., cellulose,^{25–28} lignin,^{22,29,30} starch,³¹ chitin^{24,32,33}) and platform chemicals (e.g., carbohydrates,³⁴ 5-hydroxymethylfurfural³⁵). Therefore, NPs@ILs possess high catalytic activities for the conversion of biomass resulting from the direct contact between the active sites of the metal NPs and the catalysis substrate, which is challenging to achieve using classic heterogeneous catalysts and solvents due to steric and polarity constraints associated with bio-based substrates. NP@IL catalysts also facilitate product removal and catalyst recovery during biomass conversions as the majority of transformations involve the formation of less polar and/or more volatile value-added products that have reduced solubilities in the IL phase. This allows for a facile separation of the reaction products, through decantation, extraction, or distillation, and reuse of the NP@IL catalyst. Furthermore, process control of product separation and immobilization of the metal NPs within the IL phase provides the possibility for the use of NPs@ILs in continuous flow conversions of biomass.

The molecular diversity of ILs allows for the introduction of additional functionalities into the IL structure to influence either their physical or chemical properties. Such functionalized ILs have been referred to as task-specific ILs,³⁶ in which numerous examples of Brønsted and Lewis acidic or basic ILs have been employed as recyclable acid or base catalysts.^{37–39} The combination of functionalized ILs and catalytically active NPs provides systems where different bond cleavage and formation processes can be induced by the metal surface and the IL functionality. Thus, truly multifunctional systems can be designed to enable the integration of sequential transformations into reaction cascades.^{13,40–42}

In order to fulfill their multiple roles, ILs can be used as bulk liquid phases or supported ionic liquid phases⁴³ (SILPs—ILs physisorbed^{44–46} or covalently^{47,48} attached to an inert material). The main application of the SILP concept has been in the immobilization of homogeneous metal complexes to allow catalyst recyclability and use in continuous processes.^{44–47,49} SILPs have been much less explored as stabilizers and support materials of NP catalysts;^{50–55} however, NPs@SILPs possess several advantageous properties including decreased quantities of IL,⁵⁰ improved mass transport into the IL phase⁵³ and increased stability of the NPs.^{50,51}

In the present review, we will outline the potential of NPs@ILs in the conversion of biomass substrates. NPs@ILs

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have been used in a variety of biomass transformations (*e.g.*, hydrolysis, oxidation, hydrogenation, hydrogenolysis) involving different classes of bio-based substrates (*e.g.*, glucose, glycerol, furans, phenols). We will highlight the potential advantages that NPs@ILs provide in the conversion of biomass: (1) NP stabilization; (2) tunability of the nanoparticle reactivity; (3) dissolution of a wide range of renewable resources; (4) ease of product removal to allow recycling of the NP@IL catalyst or use under continuous flow conditions; and (5) use of functionalized ILs to provide multifunctional NP@IL catalysts (Fig. 1).

The later point is of particular interest as many biomass conversion pathways comprise networks of dehydration/hydrogenation or hydrogenolysis reactions, where the combination of a metal NP and an acidic IL provides additional control parameters *via* individual modulation of the strength and concentration of both active components. The reviewed literature has been organized according to systems comprising non-functionalized and functionalized ILs in order to illustrate the significant potential multifunctional catalysis possesses in the conversion of biomass. Fig. 2 provides an overview of some of the prominent IL structures that will be highlighted in this review.

Fig. 1 Characteristics of ionic liquid-stabilized metal nanoparticles in the catalytic conversion of biomass.

2. NP@IL catalysts synthesized in non-functionalized ionic liquids

Nanoparticles in non-functionalized ILs are widely applied as catalysts for various chemical transformations of simple model compounds.^{56–63} On the other hand, modification of biomass-derived compounds catalyzed by NPs@ILs has been much less common. In this section, we will outline the use of non-functionalized ILs in the preparation of catalysts for the conversion of triglyceride- and lignocellulose-derived substrates into value-added chemicals.

NPs@ILs have been used in first generation biomass conversions involving the hydrogenation and hydrogenolysis of triglyceride-derived compounds. Polyunsaturated fatty acid methyl esters (FAMES) are prone to oxidative decomposition,

(A) Non-functionalized ILs Used in the Synthesis of NP@IL Catalysts

(B) Functionalized ILs Used in the Synthesis of NP@IL Bifunctional Catalysts

Fig. 2 Selected examples of non-functionalized and functionalized ionic liquids used in the preparation of NP@IL catalysts for the conversion of biomass.

Fig. 3 Structures of the major fatty acids present in soybean oil. Adapted from ref. 61 with permission from The Royal Society of Chemistry.

which limits the storage time and the quality of soybean-based biodiesel. One approach to improve the oxidative stability of FAMES involves their partial and selective hydrogenation to monounsaturated fatty esters (Fig. 3), which increases their stability without compromising their fuel properties. The Saurez group has used PdNPs@ILs for the partial hydrogenation of FAMES.^{64,65} In a first approach, Pd NPs were produced by *in situ* reduction of Pd(OAc)₂ in [BMIM]BF₄ (for BMIM = 1-butyl-3-methylimidazolium) under the hydrogenation conditions of FAME.⁶⁴ PdNPs@ILs (4–5 nm) possess good activities and selectivities for the formation of monounsaturated FAMES (18 : 1), while commercial Pd/C or Pd NPs synthesized in the absence of [BMIM]BF₄ produced saturated FAMES (18 : 0) as the major product (50 °C, 10 bar H₂). The IL induced selectivity to monounsaturated FAMES (18 : 1) was attributed to an increased solubility of diunsaturated FAMES (18 : 2) in [BMIM]-BF₄ compared to monounsaturated FAME (18 : 1); an observation in agreement with previous studies on the selective hydrogenation of dienes to alkenes in [BMIM]BF₄.^{66,67} Monitoring the reaction composition over time showed that PdNPs@[BMIM]BF₄ catalyzed the hydrogenation of polyunsaturated FAMES into monosaturated FAMES (18 : 1) at a fast reaction rate, while extending the reaction time did not lead to significant quantities of saturated FAMES (18 : 0) or *cis*-to-*trans* isomerization of monounsaturated FAMES. The immiscibility of FAMES in [BMIM]BF₄ allowed for a facile product separation *via* decantation and reuse of the PdNP@[BMIM]BF₄ catalyst in subsequent cycles. The catalytic activity of PdNPs@[BMIM]BF₄ was maintained over three cycles; however, a gradual catalyst deactivation occurred over seven runs.

In a second approach, the Suarez and Nome groups reported the hydrogenation of FAMES catalyzed by Pd NPs stabilized with an imidazolium zwitterionic surfactant.⁶⁵ NPs were prepared by reduction of Na₂[PdCl₄] using NaBH₄ in an aqueous solution of 3-(1-dodecyl-3-imidazolium)propanesulfonate (IL1). An aqueous solution of PdNPs@IL1 was stirred with Al₂O₃ to form a supported catalyst (PdNPs@IL1-Al₂O₃). FAME hydrogenation was performed using PdNPs@IL1-Al₂O₃ under solventless and biphasic conditions using [BMIM]NTf₂ (for ⁻NTf₂ = bis(trifluoromethanesulfonyl)imide). Under solvent-

less conditions, PdNPs@IL1-Al₂O₃ showed higher activity than commercial Pd/C for the hydrogenation of FAME to the completely saturated fatty esters (18 : 0). In the presence of [BMIM]-NTf₂, the product selectivity for PdNPs@IL1-Al₂O₃ increased towards *cis*-monounsaturated FAMES (18 : 1 *cis*) (44% selectivity; 27 °C, 75 bar, 4 h). The biphasic catalyst was recovered *via* decantation of the FAME phase and reused for four cycles without a noticeable deactivation of PdNPs@IL1-Al₂O₃.

Glycerol is another promising renewable feedstock obtained from triglycerides as a by-product of bio-diesel production.⁶⁸ Han and coworkers have examined the use of supported bimetallic RuCu NPs as catalysts for the selective hydrogenolysis of glycerol to 1,2-propanediol.⁶⁹ Bimetallic RuCu NPs were immobilized within a SILP composed of bentonite modified with 1,1,3,3-tetramethylguanidinium lactate (IL2-BEN). RuCu NPs were synthesized by wet impregnation of IL2-BEN with an aqueous solution of RuCl₃ and Cu(NO₃)₂, followed by reduction under an atmosphere of H₂. A series of RuCuNPs@IL2-BEN were synthesized and evaluated in the aqueous phase hydrogenolysis of glycerol, in which the molar ratio of Ru : Cu had a significant influence on the activity and selectivity of the bimetallic catalyst. The ratio of 3 : 1 (Ru : Cu) showed the best balance between the activity and the selectivity towards 1,2-propanediol and under optimal conditions (230 °C, 80 bar H₂, 18 h) complete conversion of glycerol was obtained with a 1,2-propanediol selectivity of 86%. RuCuNPs@IL2-BEN was recycled for at least five cycles without losing the catalytic activity or selectivity. A catalyst synthesized in the absence of IL2, RuCuNPs@BEN, showed reduced activity, selectivity and stability, and thus illustrated the significant role of IL2 in stabilizing catalytically active RuCu NPs.

NP@IL catalysts have been applied in second-generation biomass conversion processes involving the transformation of lignocellulose-derived substrates. Chen and coworkers reported the Lewis acid catalyzed dehydration of glucose to 5-hydroxymethylfurfural (HMF) using Cr(0) NPs in [EMIM]Cl (EMIM = 1-ethyl-3-methylimidazolium) (Scheme 1).⁷⁰ *In situ* synthesized Cr NPs (2.3 nm) prepared by decomposition of Cr(CO)₆ in [EMIM]Cl under the glucose dehydration conditions yielded 49% of HMF (120 °C, 6 h), while under identical conditions the benchmark catalyst (a homogeneous catalyst com-

Scheme 1 Glucose dehydration catalyzed by Cr NPs formed by decomposition of Cr(CO)₆ in [EMIM]Cl. Reprinted with permission from ref. 67, Copyright 2013 John Wiley and Sons.

Scheme 2 Condensation and selective hydrogenation of biomass-derived furans, furfuralacetone (**16**) and tris(5-methylfuran-2-yl)-methane (**17**), using NP@IL catalysts.^{80,81}

posed of CrCl_2 in $[\text{EMIM}][\text{Cl}]$ ⁷¹ produced a lower yield of HMF (45%). In order to validate that $\text{Cr}(0)$ NPs are the active catalytic species, *ex situ* Cr NPs (3.6 nm) were prepared in $[\text{BMIM}]\text{BF}_4$ by thermal degradation *via* microwave irradiation, in which $\text{CrNPs}@\text{[BMIM]BF}_4$ reached higher yields of HMF (54%). Poisoning experiments with 1,10-phenanthroline indicated surface-like catalytic species for $\text{CrNPs}@\text{[BMIM]X}$ and single-site active species for the CrCl_2 -based benchmark catalyst, and thus provided evidence that $\text{Cr}(0)$ NPs can efficiently catalyze the dehydration of glucose to HMF.

Non-functionalized ILs have also been used to stabilize NP catalysts for the hydrogenation of lignocellulose-derived substrates. Furan-based platform chemicals (*e.g.*, furfural, HMF) are attractive biomass molecules as their carbon content can be increased *via* aldol condensation and coupled with selective hydrogenation to produce value-added chemicals and potential biofuels.^{72–76} Furfuralacetone (**16**) can be synthesized by the aldol condensation of furfural and acetone and has been a popular strategy to transform pentose platform chemicals into C_8 -products (Scheme 2A).⁷² C–C coupling of hemicellulose-derived furans can also be achieved *via* the electrophilic aromatic substitution of 2-methylfuran.^{77,78} For example, the condensation of 5-methylfurfural with 2-methylfuran yields product **17**, in which selective aromatic substitution occurs at the 5-position of the 2-methylfuran rings (Scheme 2B).⁷⁹

Leitner and coworkers have studied the hydrogenation of furfuralacetone (**16**) using Ru NPs (2–3 nm) prepared by H_2 reduction of $\text{Ru}(\text{2-methylallyl})_2(\text{cod})$ in a variety of imidazolium ILs (Scheme 2A).⁸⁰ The catalytic activity and selectivity of $\text{RuNPs}@\text{ILs}$ in the hydrogenation of **16** were dependent on the nature of the IL. The catalytic behavior of $\text{RuNPs}@\text{[EMIM]X}$ was influenced by the anion such that $[\text{EMIM}]\text{Br}$ favoured product **16a**, $[\text{EMIM}]\text{MeCO}_2$ produced a mixture of **16a–d**, and $[\text{EMIM}]\text{NTf}_2$ or $[\text{EMIM}]\text{BF}_4$ preferred the fully saturated product **16c**. The most active Ru NPs were stabilized by $[\text{C}_{12}\text{MIM}]\text{NTf}_2$ (for C_{12}MIM = 1-dodecyl-3-methylimidazolium) which obtained complete conversion of **16** to the saturated product **16c** (120 °C, 120 bar H_2 , 2 h). The reaction network for

substrate **16** was evaluated using $\text{RuNPs}@\text{[C}_{12}\text{MIM}]\text{NTf}_2$ under mild conditions (60 °C, 60 bar H_2). The hydrogenation of **16** occurred as a consecutive reaction involving the initial hydrogenation of the C=C bond to form **16a**, followed by aromatic hydrogenation to **16b** and finally hydrogenation of the C=O bond to a completely saturated product **16c** (Fig. 4). $\text{RuNPs}@\text{[C}_{12}\text{MIM}]\text{NTf}_2$ could be reused for at least five cycles without losing activity after extraction of **16c** using supercritical CO_2 .

Bell and coworkers have investigated the hydrogenation of the furan-based substrate **17** using NP@IL catalysts (Scheme 2B).⁸¹ Pd NPs were immobilized on a SILP composed of 1-propyl-3-octylimidazolium chloride tethered to silica (SILP3). Pd NPs (2.6 nm) were produced by wet impregnation of the SILP with a solution of PdCl_2 , reduction of $\text{Pd}(\text{II})$ to $\text{Pd}(0)$ using NaBH_4 and exchange of the SILP anion with BF_4^- , NTf_2^- or PF_6^- . $\text{PdNPs}@\text{SILP3}$ was tested in the selective hydrogenation of **17** towards the completely saturated product **17c**, in which the catalytic activity and selectivity were dependent on the SILP anion. $\text{PdNPs}@\text{SILP3-X}$ (for $\text{X} = \text{Cl}^-, \text{BF}_4^-, \text{NTf}_2^-$) were active catalysts; however, they provided a mixture of products **17a–e**. The most active and selective catalyst,

Fig. 4 Reaction network for the hydrogenation of furfuralacetone (**16**) catalyzed by $\text{RuNPs}@\text{[C}_{12}\text{MIM}]\text{NTf}_2$. Reproduced from ref. 77 with permission from The Royal Society of Chemistry.

PdNPs@SILP3-PF₆, produced **17c** with 78% selectivity (75 °C, 14 bar H₂, 10 h), which was significantly higher than commercial Pd/C under the same conditions (39% selectivity of **17c**). Furthermore, PdNPs@SILP3-PF₆ could be reused for the hydrogenation of **17** under neat conditions for at least five runs without a noticeable loss in activity; although, the catalytic selectivity decreased due to NP growth (~3 nm).

Levulinic acid (LA), a platform chemical obtained from the C₆-fraction of lignocellulose, is another promising starting material for the creation of a wide variety of value-added chemicals. The hydrogenation/dehydration of LA leads to the formation of γ -valerolactone (GVL), which can be used as a biofuel, solvent or food additive.^{82,83} Selva and coworkers have employed a RuNP@IL catalyst in a triphasic system composed of water/IL/iso-octane for the hydrogenation of LA to GVL.⁸⁴ The hydrogenation reaction took place in the water phase, while the IL allowed for catalyst segregation and iso-octane facilitated separation of the aqueous product phase (Fig. 5). [N_{8,8,8,1}]X and [P_{8,8,8,1}]X (for N_{8,8,8,1} = trioctylmethylammonium, P_{8,8,8,1} = trioctylmethylphosphonium, X = Cl⁻, NTf₂⁻) were the most effective ILs due to their low solubility in water. Ru NPs (2–3 nm) were synthesized *in situ* from RuCl₃ using a triphasic system of water/[N_{8,8,8,1}]Cl/iso-octane for the hydrogenation of LA, in which LA was converted to GVL with a yield of 65% (150 °C, 35 bar H₂, 16 h). Upon removal of the aqueous product phase, the RuNP@[N_{8,8,8,1}]Cl/iso-octane phase was recycled in six cycles, in which the GVL yield improved to 99% and was maintained without any loss of activity. The catalytic activity of RuNPs@ILs was lower than commercial Ru/C in the water/[P_{8,8,8,1}]NTf₂/iso-octane triphase as the conversion of LA to GVL (>70%) was achieved under much milder conditions (100 °C, 35 bar H₂, 1 h) and was also reused for eight recycles without any loss of activity.

Lignin represents an attractive feedstock for the production of renewable aromatic substrates.^{85,86} Lignin has also been shown to be soluble in ILs^{22,29,30} and thus NPs@ILs are suitable catalysts for the conversion of lignin. Zhu and coworkers reported the oxidation of lignin using PdNPs@ILs (Scheme 3).⁸⁷ Pd NPs (2.4 nm) were prepared from H₂PdCl₄ in [BMIM]MeSO₄ (for MeSO₄⁻ = methylsulfate) by a polyol reduction method. PdNPs@[BMIM]X (for X = MeSO₄⁻, PF₆⁻)

Scheme 3 Lignin oxidation to aromatic aldehydes catalyzed by PdNP@IL catalysts.⁸⁷

were combined with *N*-pentyl-4-methylpyridinium iron bis(dicarbollide) as a co-catalyst to achieve the oxidation of benzyl alcohol model substrates and lignin. Substituted benzyl alcohols were oxidized to benzaldehydes in yields >77% (120 °C, 4 bar O₂, 18 h). The oxidation of lignin was performed under identical reaction conditions and provided 72% conversion of lignin into aromatic aldehydes after 18 h. The major products formed from the oxidation of lignin were syringaldehyde, vanillin and *p*-hydroxybenzaldehyde. The recovered catalyst system was recycled at least three times showing only a 4% decrease in activity after the fourth run.

3. NP@IL bifunctional catalysts synthesized in functionalized ionic liquids

Functionalized ILs have been employed in the synthesis of metal NPs,²¹ in which functionalized ILs have been used to (1) increase the solubility of a NP stabilizer or substrate in an IL phase;⁸⁸ (2) improve the stability of metal NPs by incorporation of a metal binding moiety;^{89–93} (3) immobilize NPs onto a support material;^{94,95} and (4) form bifunctional catalysts through functionalization with an organic moiety that participates in the chemical reaction. In the conversion of biomass, the combination of an acid and a metal catalyst provides bifunctional catalysts for the deoxygenation of platform chemicals through multiple acid (*e.g.*, hydrolysis, dehydration, condensation) and metal (*e.g.*, hydrogenation, hydrogenolysis) catalyzed reactions in a single-pot process. In this section we will highlight the use of acid-functionalized ILs (Fig. 2B) in the preparation of bifunctional catalysts for the conversion of lignocellulosic substrates into value-added chemicals.

Zhu and coworkers have reported a boronic acid-functionalized IL4 in the formation of a bifunctional catalyst for the conversion of cellulose into hexitols.⁴¹ A boronic acid-functionalized IL was selected as an IL soluble catalyst for the depolymerization and hydrolysis of cellulose into glucose. The combination of IL4 and metal NPs allowed for the conversion of cellulose into glucose and the subsequent hydrogenation of glucose into sorbitol in a single-pot reaction (Scheme 4). Ru

Fig. 5 Photographs of the triphasic catalyst system (water/[N_{8,8,8,1}]Cl/iso-octane) for the hydrogenation of levulinic acid to γ -valerolactone using RuNPs@[N_{8,8,8,1}]Cl before (left) and after catalysis (right). Reprinted with permission from M. Selva, M. Gottardo and A. Perosa, *ACS Sustainable Chem. Eng.*, 2013, 1, 180–189. Copyright 2012 American Chemical Society.

Scheme 4 Catalytic conversion of cellulose into hexitols using the bifunctional catalysts composed of Ru NPs stabilized in a solution of IL4 in [BMIM]Cl or [THTdP]DBS Reprinted with permission from ref. 38, Copyright 2009 John Wiley and Sons.

NPs (4.0 nm) were synthesized in a solution of IL4 and [BMIM]-Cl or [THTdP]DBS (for THTdP = trihexyltetradecylphosphonium, DBS = dodecylbenzene sulfonate). In the absence of IL4 and Ru NPs, a very low conversion of cellulose was observed (<5%). A solution of IL4 and [BMIM]Cl catalyzed the hydrolysis of cellulose into glucose (87% selectivity to glucose). The bifunctional catalyst composed of RuNPs@IL4-[BMIM]Cl was an effective catalyst for the conversion of cellulose to sorbitol using a variety of hydrogen sources (*i.e.*, formic acid, sodium formate, hydrogen), in which the best results were obtained using sodium formate as a hydrogen donor (94% selectivity to sorbitol; 80 °C, 5 h). Similar results were obtained for RuNPs@IL4-[THTdP]DBS (93% selectivity to sorbitol). RuNPs@IL4-[BMIM]Cl was recycled in subsequent cycles after removal of the reaction mixture by water extraction. The bifunctional catalyst was employed for five runs using sodium formate as a hydrogen source, in which the activity of the catalyst was maintained over five cycles and the Ru leaching into the aqueous phase was <3 ppm.

One strategy towards the deoxygenation of biomass substrates involves the combination of an acid and metal species in a single-pot reaction. This type of bifunctional catalyst can reduce the oxygen content of biomass compounds through reactions such as dehydration, condensation, hydrogenation and hydrogenolysis.^{13,40,42,96–98} This approach has been shown to be an effective route toward the deoxygenation of phenolic substrates as model compounds for the depolymerization of lignin and the upgrading of bio-oils (Scheme 5).

Dyson and coworkers first reported the use of Brønsted acidic functionalized ILs 5–8 in the formation of a bifunctional catalyst for the deoxygenation of phenolic substrates.⁴⁰ Their bifunctional catalyst combined together a Brønsted acidic functionalized IL with metal NPs in an IL solvent to catalyze the deoxygenation of phenol to cyclohexane (Scheme 5). A series of Brønsted acid-functionalized ILs were prepared and

Scheme 5 Reaction pathway for the deoxygenation of phenol to cyclohexane using bifunctional catalysts composed of acidic ILs and metal NPs (metal catalyzed reactions = blue, acid catalyzed reactions = red).

were initially evaluated in the dehydration of cyclohexanol to cyclohexene. The most effective acid catalysts 5–8 contained a sulfonic acid moiety functionalized on the imidazolium alkyl chain and was accompanied by a trifluoromethanesulfonate anion ([−]OTf). The acidity of 5–8 increased as the length of the *N*-alkyl chain decreased and IL8 showed the highest activity for the dehydration of cyclohexanol to cyclohexene. Acidic IL5 was combined with Rh, Ru, Pd and Pt NPs stabilized by an IL-like copolymer, poly(1-vinyl-3-butylimidazolium chloride-co-*N*-vinyl-2-pyrrolidone), in [EMIM]X as a reaction solvent (for [−]X = [−]BF₄, [−]NTf₂) to catalyze the deoxygenation of phenol to cyclohexane. The combination of Rh NPs (2–3 nm) with IL5 in [EMIM]NTf₂ provided the most effective bifunctional catalyst for the production of cyclohexane (84% cyclohexane selectivity; 130 °C, 40 bar H₂, 4 h). The activity of the bifunctional catalyst was further improved by using the most acidic IL8 in combination with Rh NPs in [EMIM]NTf₂, in which a similar activity and selectivity was obtained at a lower reaction temperature (80% cyclohexane selectivity; 110 °C, 40 bar H₂, 4 h).

The deoxygenation of phenolic compounds has also been reported by Chen and coworkers employing a sulfonate-functionalized IL-like copolymer (IL9).⁹⁶ The bifunctional catalyst was composed of copolymer IL9 and H₃PO₄ as the acid catalyst, and water-soluble Ru NPs as the metal catalyst (2.4 nm) (Scheme 6). RuNPs@IL9-H₃PO₄ was used

Scheme 6 Deoxygenation of phenol using an aqueous solution of RuNPs@IL9-H₃PO₄ before (right) and after (left) catalysis. Reprinted with permission from ref. 93, Copyright 2013 John Wiley and Sons.

for the hydrogenation of phenol in aqueous solution, in which the selectivity of the reaction could be tuned by altering the reaction temperature. The hydrogenation product, cyclohexanol, was obtained with >99% selectivity at 160 °C, while the deoxygenation product, cyclohexane, was produced in >99% at 200 °C (50 bar H₂, 3 h). Product separation of cyclohexane was achieved by decantation, due to the immiscibility of cyclohexane in water, and the aqueous RuNPs@IL9-H₃PO₄ phase was reused in further cycles. The activity of the bifunctional catalyst was maintained over three runs; however, the long-term stability of the bifunctional catalyst was limited by the growth of the Ru NPs (3.8 nm after five cycles).

Xu *et al.* have developed a supported bifunctional catalyst for the deoxygenation of phenolic substrates.⁹⁷ Acidic IL10 was immobilized onto montmorillonite (IL10-MMT) *via* ion-exchange and/or adsorption to produce a SILP, which acted as both an acid catalyst and support material for metal NPs. Ru NPs were synthesized on IL10-MMT to provide small and well-dispersed NPs (1.3 nm), which were used in the deoxygenation of phenol in aqueous solution. RuNPs@IL10-MMT catalyzed the deoxygenation of phenol to cyclohexane (100% cyclohexane selectivity; 200 °C, 50 bar H₂, 1 h). The recyclability of this bifunctional catalyst was examined over four cycles, in which only a slight decrease in the conversion of phenol and the selectivity to cyclohexane was observed. The reduced activity and selectivity of RuNPs@IL10-MMT was attributed to growth of the Ru NPs (2.2 nm) and desorption of IL10 from the MMT support.

Brønsted acid-functionalized ILs have also been explored in the formation of bifunctional catalysts for the deoxygenation of lignocellulose platform chemicals.^{13,98} Julis and Leitner reported bifunctional catalysts composed of Ru NPs stabilized in acidic ILs 11–14 for the selective deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (**16c**) to 1-octanol (**18b**) (Scheme 7).¹³ The reaction pathway for the deoxygenation of **16c** involved a dehydration/hydrogenation to 2-butyltetrahydrofuran (**18a**) and a selective hydrogenolysis of the tetrahydrofuran ring to produce alcohol **18b**.

Ru NPs were synthesized in a solution of acidic ILs 11–14 in [EMIM]NTf₂ to provide a bifunctional catalyst required for the deoxygenation of **16c**. The RuNPs@IL13 (a carboxylic acid-functionalized IL) did not possess activity for this transformation, while Ru NPs stabilized in sulfonic acid-functio-

Scheme 8 Integrated multi-step synthesis of aliphatic C₈-products from bio-based platform chemicals furfural and acetone. Reprinted with permission from ref. 12, Copyright 2012 John Wiley and Sons.

nalized IL11, IL12 and IL14 were active catalysts for the deoxygenation of **16c**. RuNPs@IL14 provided the most active bifunctional catalyst toward the formation of alcohol **18b** (42%) and aliphatic ether **18c** (34%) (C₈-OLs = 76%) (150 °C, 120 bar H₂, 15 h). This transformation was also shown to be possible directly from the bio-based platform chemicals, furfural and acetone; however, to achieve this multi-step reaction Ru/C was used as the metal catalyst to impart long-term stability to the metal catalyst. A C₈-OL yield of 93% was obtained in a one-pot, two-step reaction starting from **16**, while a 52% yield of C₈-OLs was produced in a one-pot, three-step reaction starting from furfural and acetone (Scheme 8).

Luska *et al.* have extended the research on the deoxygenation of **16c** by developing supported bifunctional catalysts.⁹⁸ Design of the bifunctional catalyst involved the anchoring of an acid-functionalized imidazolium IL onto silica as an inorganic matrix to provide both an acid catalyst and stabilization medium for Ru NPs. Combination of a sulfonic acid-functionalized IL with a non-functionalized IL allowed for the acidity of SILP15 to be molecularly controlled by altering the quantity of acid moieties grafted onto the silica. The quantity of sulfonic acid moieties immobilized onto silica (defined as SILP acidity = IL-CH₂SO₃H/[IL-CH₂SO₃H + IL-CH₃]) (Fig. 2B) was varied to provide a range of SILP acidities (SILP15-0.33, SILP15-0.66 and SILP15-1.00). Ru NPs were synthesized within SILP15 to provide bifunctional catalysts containing small and well-dispersed Ru NPs (1.7 nm). The bifunctional catalysts, RuNPs@SILP15, were used in the deoxygenation of **16c**, in which the catalytic activity and selectivity of the catalyst were influenced by the acidity of SILP15. An increase in the SILP acidity increased the catalytic activity of the bifunctional catalyst such that RuNPs@SILP15-1.00 produced 98% C₈-OLs during the first cycle of catalysis and only a slight decrease in yield was observed after the third cycle of catalysis (C₈-OL yield = 88%) (150 °C, 120 bar H₂, 4 h). Optimization of the SILP acidity and the reaction parameters allowed for control of the deoxygenation selectivity toward the formation of different classes of value-added products: cyclic ethers (**18a**), primary alcohols (**18b**) and aliphatic ethers (**18c**) (Scheme 9).

Scheme 7 Selective deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (**16c**) toward C₈-mono-oxygenates as value-added products from lignocellulosic biomass.^{13,98} Adapted with permission from ref. 12, Copyright 2012 John Wiley and Sons.

Scheme 9 Synthetic pathway for the selective deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (**16c**) toward different classes of value-added chemicals, cyclic ethers (**18a**), primary alcohols (**18b**) and aliphatic ethers (**18c**) catalyzed by RuNPs@SILP15. Reproduced from ref. 95 with permission from The Royal Society of Chemistry.

4. Conclusions and outlook

NPs@ILs are promising catalysts for the conversion of triglyceride- and lignocellulose-derived substrates as their catalytic properties can be tailored by selecting a suitable combination of IL and metal NP components. NPs@ILs are active catalysts for the hydrolysis, oxidation, hydrogenation and hydrogenolysis of biomass to value-added chemicals and fuels. ILs provide a stabilization matrix that allows an intimate contact between the active sites of the NP and the catalysis substrate, but also provides a means to control the surface reactivity of the metal NPs. Furthermore, ILs facilitate an effective separation of the products as the majority of biomass transformations result in the formation of less polar and/or more volatile compounds. Such process control provides an opportunity to recycle and/or implement NP@IL catalysts into continuous flow operation.

Functionalized ILs have allowed for the formation of multifunctional NP@IL catalysts to achieve multi-step transformations in a single-pot reaction. Multifunctional NP@IL catalysts based on acid-functionalized ILs have been employed for the direct conversion of cellulose to sorbitol and for the dehydration/hydrogenation of lignocellulose platform chemicals. These multifunctional catalysts have illustrated how iterative acid and metal catalyzed reactions allow for the hydrodeoxygenation of bio-based substrates. Functionalized ILs also provide a molecular design tool by which the catalytic activity of a heterogeneous-based catalyst can be tailored, in which incorporation of other functional moieties into the IL structure may provide new opportunities for the conversion of biomass.

The majority of NP@IL catalysts reported thus far involve the formation of colloidal NPs in an IL solvent. In these catalyst systems, ILs play the dual role of a reaction solvent and a NP stabilizer, in which product removal allows for the reuse of the NP@IL phase in subsequent cycles. The stabilization provided by ILs allows for the production of highly active catalysts; however, the long-term stability of these colloidal NP@IL cata-

lysts can be limited under the catalytic conditions required for biomass transformations (*e.g.*, high pressures and temperatures, in the presence of water).⁹⁶ One method to improve the stability of NP@IL catalysts has been through the use of SILPs, by which immobilization of colloidal NPs onto a support restricts contact between particles and reduces NP growth and aggregation.^{50,51} To date, NP@SILP catalysts have only been used under batch conditions; however, NPs@SILPs have significant potential in the creation of continuous flow processes with increased space-time-yields, enhanced process control and reduced solvent use or waste production.⁹⁹ SILPs have demonstrated efficiencies as supports for homogeneous catalyzed biomass conversions under continuous flow conditions, in which supercritical CO₂ is an optimal mobile phase to prevent metal or IL leaching due to the high polarity of biomass substrates.^{49,100–102}

There exists many further opportunities for the use of NP@IL catalysts in the conversion of biomass. One advantage in using ILs for the processing of biomass involves their ability to dissolve biopolymers, although only two examples have been reported in which NPs@ILs have been used in the direct conversion of biopolymers.^{41,87} Novel bifunctional NP@ILs catalysts can be designed to allow for the depolymerization and subsequent conversion of intermediates to value-added chemicals from various types of biopolymers (*e.g.*, cellulose, lignin, chitin). However, there exists a debate on the large-scale use of ILs in the chemical industry due to their high cost, long-term stability and potential toxicity.²⁸ To this end, SILPs provide an opportunity to reduce the amount of IL required in the formation of NP@IL catalyst systems. NP@SILPs could be used in the conversion of biomass employing aqueous or green organic solvents, especially in the context of their use in continuous flow processes.

In this review we have outlined the early progress and conceptual approach towards the use of NPs@ILs for the conversion of biomass into chemicals and fuels. As the number of catalysis studies investigating the use of NP@IL catalysts in the field of biomass increases, full characterization of these catalysts both before and after catalysis becomes increasingly necessary. Biomass conversions often occur in the presence of water and require the use of high temperatures and pressures, thus the NP size, shape and distribution must be measured to evaluate the stability of NPs@ILs under these conditions. While TEM is an important technique used to determine the NP size and distribution, other tools should be used whenever possible (*e.g.*, XRD, SAXS) as they provide complementary and very valuable insight into the physical properties of the NPs.¹⁷ Identification of the NP composition (*e.g.*, oxidation state, presence of an oxide layer) and the interaction between the IL and the metal surface is crucial for the understanding of their performance and can be determined using XPS, EDX and EXAFS.¹⁷ Lastly, as bio-based substrates are highly polar compounds, biomass transformations have an increased risk of metal and IL dissolution into the reaction mixture and thus ICP of the catalyst and product phases should be conducted to evidence any possible leaching. Control experiments such as

the hot filtration test and mercury poisoning also allow for the discrimination between a homogeneous and a heterogeneous active species. A complete characterization of NPs@ILs, once applied under conditions for biomass conversion, will allow for the rational development of further generation of catalysts and for an evaluation of the feasibility of using this class of catalysts for practical implementation.

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