Chemical Science

EDGE ARTICLE



Cite this: DOI: 10.1039/c4sc02033b

Bifunctional nanoparticle-SILP catalysts (NPs@SILP) for the selective deoxygenation of biomass substrates[†]

Kylie L. Luska,^a Jennifer Julis,^{ac} Eli Stavitski,^d Dmitri N. Zakharov,^e Alina Adams^a and Walter Leitner^{*ab}

Ruthenium nanoparticles were immobilized onto an acidic supported ionic liquid phase (RuNPs@SILP) in the development of bifunctional catalysts for the selective deoxygenation of biomass substrates. RuNPs@SILPs possessed high catalytic activities, selectivities and recyclabilities in the hydrogenolytic deoxygenation and ring opening of C_8 - and C_9 -substrates derived from furfural or 5-hydroxymethylfurfural and acetone. Tailoring the acidity of the SILP through the ionic liquid loading provided a molecular parameter by which the catalytic activity and selectivity of the RuNPs@SILPs were controlled to provide a flexible catalyst system toward the formation of different classes of value-added products: cyclic ethers, primary alcohols or aliphatic ethers.

Received 9th July 2014 Accepted 27th August 2014

DOI: 10.1039/c4sc02033b

www.rsc.org/chemicalscience

Introduction

Declining petrochemical resources and climate change are a significant challenge, but at the same time a remarkable opportunity for the chemical industry to develop and implement novel sustainable synthetic routes for the production of fine chemicals and fuels from renewable resources.¹⁻⁶ Lignocellulosic materials, such as agricultural and forestry residues, are a viable feedstock for the chemical industry as they represent the largest source of terrestrial carbon which is renewable in short enough time frames to be useful for mankind. The utilization of lignocellulose requires the development of effective catalytic transformations to selectively generate a variety of value-added products from carbohydrate-derived platform chemicals.⁷⁻⁹

Our group has developed the concept of "pathway design" to identify catalytic routes to tailor-made chemicals in analogy to the retrosynthetic analysis used by organic chemists.^{8,10,11} After successful application to the development of molecular catalysts for the synthesis of C_5 -lactones, diols and cyclic ethers, we recently applied this strategy to the synthesis of 1-octanol from furfural and acetone.^{9,12} The production of medium chain alcohols from lignocellulosic biomass¹³ opens a new approach to important industrial chemicals in the production of detergents, surfactants, perfumes and flavours.¹⁴ Furthermore, medium chain alcohols have been identified as attractive 3rd generation biofuels with highly desirable combustion properties.^{15,16}

In general, the pentose- and hexose-derived platform chemicals furfural and 5-hydroxymethylfurfural can be upgraded to higher carbon intermediates (C_8 – C_9) through an aldol condensation with acetone (a ketone that can be synthesized from biomass feedstocks through Acetone–Butanol–Ethanol (ABE) fermentation).^{17,18} The complete deoxygenation of these furanic substrates has been used to synthesize alkanes as biobased surrogates of diesel and jet fuels.^{18–24} In contrast, their selective deoxygenation toward C_8 - and C_9 -oxygenates has been challenging to accomplish,^{20,25–32} as it requires judicious control over a complex network of multiple acid and metal catalyzed reactions (*i.e.* dehydration, hydrogenation, hydrogenolysis).^{3,33} The combination of an acid and metal component in a bifunctional catalyst material offers a potential strategy to address this challenge.

In our present work, we describe a molecular approach to the preparation of tuneable bifunctional catalytic materials as a means to control the C–O deoxygenation of biomass substrates towards different classes of value-added products: cyclic ethers, alcohols and aliphatic ethers (Scheme 1).

The design of our bifunctional catalysts involved the immobilization of an acid-functionalized imidazolium ionic liquid (IL) onto silica as inorganic matrix to provide both an



View Article Online

^aInstitut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany. E-mail: leitner@itmc.rwth-aachen.de; Fax: +49-241-80-22177; Tel: +49-241-80-26481

^bMax-Planck-Institut für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany ^cEvonik Industries AG, Paul-Baumann-Strasse 1, 45772 Marl, Germany

^dPhoton Sciences Directorate, Brookhaven National Laboratory, Upton, NY, 11973, USA

^eCenter for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, 11973, USA

[†] Electronic supplementary information (ESI) available: Full synthesis and characterization data (NMR and HRMS) of ILs and catalytic substrates, additional FTIR, ²⁹Si MAS NMR, XANES and EXAFS data of SILPs and RuNPs@SILPs, complete catalysis results. See DOI: 10.1039/c4sc02033b



Scheme 1 Retrosynthetic analysis toward the synthesis of C₈- and C₉-oxygenates as value-added products from lignocellulosic biomass.



Fig. 1 Bifunctional catalysts composed of an acid-functionalized supported ionic liquid phase and ruthenium nanoparticles (RuNPs@SILP) employed for the selective hydrogenolytic deoxygenation of biomass substrates (for $R = -CH_2SO_3H$, $-CH_3$).

acid catalyst and stabilization medium for ruthenium nanoparticles (Ru NPs) generated from organometallic complexes as precursors (Fig. 1). Immobilized ILs are generally referred to as supported ionic liquid phases (SILPs) and involve either the physisorption³⁴⁻³⁷ or covalent attachment^{37,38} of IL structures onto a support material. The major application of SILPs has been as supports for the immobilization of homogeneous metal complexes to allow for catalyst recovery, reuse and employment under continuous flow conditions.^{34-36,38,39} Task-specific ILs⁴⁰ have also been employed in the formation of SILPs to provide heterogenized ILs as metal-free organocatalysts of various organic transformations.37,41-46 A much less explored application of SILPs has been as supports in the formation of metal nanoparticle (NP) catalysts,47-52 even though unsupported ILs have been shown to be effective solvents and stabilizers in the formation of stable suspensions of catalytically active metal NPs.53-60

Results and discussion

Synthesis of supported ionic liquid phases and bifunctional catalysts

The syntheses of SILPs were achieved through the condensation of an acid-functionalized IL, [1-(4-sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (1), and a non-functionalized IL, [1-butyl-3-(3-triethoxysilylpropyl)-imidazolium]NTf₂ (2), with dehydroxylated SiO₂ (see ESI† for complete SILP characterization data). Combination of an acid-functionalized IL 1 and a non-functionalized IL 2 allowed for the quantity of sulfonic acid moieties grafted onto SiO₂ (defined herein as the SILP acidity or



Sample	Acid loading ^a	Total IL loading ^b (mmol IL per g SiO ₂)	Surface area (m ² g ⁻¹)	Pore radius (Å)
SiO ₂	_	_	344	48.3
SILP-0.00	_	0.78	208	35.7
SILP-0.33	0.33	0.81	182	40.1
SILP-0.66	0.66	0.85	181	40.5
SILP-1.00	1.00	0.88	146	45.2
RuNPs@SILP-1.00	1.00	0.88	151	46.3

^{*a*} Acid loading = IL 1/[IL 1 + IL 2]. ^{*b*} Total IL loading = theoretical IL loading - recovered residual IL (for theoretical IL loading = 0.88 mmol IL per g SiO₂).

acid loading = IL 1/[IL 1 + IL 2]) to be varied between 0.00 and 1.00 with respect to the total loading of IL (Table 1). Characterization of the SILPs using Brunauer-Emmett-Teller (BET) analysis showed a decrease in the surface area and pore radius in comparison to dehydroxylated SiO₂, which is an effect that has been previously reported in the literature for the grafting of ILs onto SiO₂.^{46,61} DRIFT FTIR analysis (Fig. S10[†]) of the SILPs revealed signals resulting from the functionalization of ILs 1 and 2 on SiO₂ including the C-H stretch of the imidazolium ring and the aliphatic chain (3160 and 2947 cm^{-1}) and the symmetric ring stretch of the imidazolium moiety (1566 and 1452 cm⁻¹).43,46,61</sup> Solid-state ²⁹Si MAS NMR of SILP-1.00 (Fig. S11 and Table S1[†]) revealed two different types of Si bonding: (1) tetra-functionalized (Q) signals at -110 (Q₄ = $(Si(OSi)_4)$ and -102 ppm $(Q_3 = (Si(OSi)_3OH);$ and (2) tri-functionalized (T) signals at -67 (T₃ = (R-Si(OSi)₃) and -57 ppm $(T_2 = (R-Si(OSi)_2OR', \text{ for } R' = H \text{ or } Et).^{46,61,62}$ The T_3 and T_2 signals correspond to the Si atoms of IL 1 bound to the SiO₂ surface and thus proved that IL 1 was covalently attached to the silica material.

The synthesis of Ru NPs immobilized on SILPs (RuNPs@SILPs) involved the wet impregnation of the SILP (0.50 g) with a solution of [Ru(2-methylallyl)₂(cod)] (5.1 mg, 0.016 mol) in dichloromethane (DCM) (5 mL) (Scheme 2). Upon addition of the [Ru(2-methylallyl)₂(cod)] solution, the SILP transformed from a white to a bright yellow colour, which indicated the adsorption of the Ru precursor into the SILP. Upon evaporation of the solvent *in vacuo*, the impregnated SILP powder was subjected to an atmosphere of H_{2(g)} (100 bar) at 100 °C for 16 h. Under these conditions, the bright yellow powder turned black in colour and signified the formation of Ru NPs. Characterization of RuNPs@SILP-1.00 showed the formation of small, well-dispersed Ru NPs (1.7 \pm 0.4 nm) by STEM (Fig. 3a) and a Ru loading of 0.25 wt% as determined by ICP.⁶³ Furthermore, BET



Scheme 2 Synthetic pathway and photographs of ruthenium nanoparticles immobilized on supported ionic liquid phases (RuNPs@SILPs).

analysis of RuNPs@SILP-1.00 indicated that the synthesis of Ru NPs within the SILP did not affect the textural properties of the SILP (Table 1). Formation of small and well-dispersed Ru particles thus demonstrated the ability of the SILPs to stabilize metal NPs.

Bifunctional catalysis in the hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol (3)

Whereas the saturation of the C=C and C=O bonds of the primary condensation product of furfural and acetone is readily achieved by hydrogenation over conventional heterogeneous catalysts,⁹ the deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (3) comprises a complex reaction network of acid and metal catalyzed transformations as outlined in Scheme 3.9 In the presence of an acid catalyst, self-etherification and isomerization of substrate 3 can occur. The etherification equilibrium is reversed as the deoxygenation of 3 takes place at the secondary OH group to form 2-butyltetrahydrofuran (4) that may isomerize to 2-propyltetrahydropyran (5). Selective ring opening of the tetrahydrofuran ring of 4 by hydrogenolysis at the secondary C-O bond produces the linear primary alcohol 1-octanol (6), which under acidic conditions can form 1,1-dioctylether (7) via self-etherification. In the present study, ethyloctylether (8) was also observed in small quantities as a result of the etherification of 6 with EtOH, in which the remaining R-Si(OSi)₂OEt moieties within the SILP introduced EtOH equivalents into the system. Finally, complete deoxygenation of 3 can occur to form *n*-octane (9). The RuNPs@SILP bifunctional catalysts were investigated for their potential to allow control of this reaction network in



Scheme 3 Reaction network for the deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (3) catalyzed by RuNPs@SILPs.



Fig. 2 Reaction profile for the hydrogenolysis of **3** using (a) RuNPs@SILP-0.33 and (b) RuNPs@SILP-0.66 (for substrate **3** = orange **II**, cyclic ethers (**4** + **5**) = green \blacklozenge , alcohol **6** = blue \divideontimes , aliphatic ethers (**7** + **8**) = purple \bigcirc , others (isomers + condensation products of **3**) = red **A**, C₈-OL yield (**6** + **7** + **8**) = pink \blacklozenge). Reaction conditions: [Ru] (0.016 mmol), SILP (0.5 g), [EMIM]NTf₂ (2.9 mL) (for [EMIM]NTf₂ = 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide), substrate (1.6 mmol), H₂ (120 bar), 150 °C.

the selective formation of the oxygenated products, whereby the combined yield of the linear C_8 -alcohol derivatives was defined as the C_8 -OL yield (C_8 -OL = 1-octanol (6) + 1,1-dioctylether (7) + ethyloctylether (8)).

The reaction profiles for the deoxygenation of 3 using RuNPs@SILP catalysts at 0.33 and 0.66 acid loadings are shown in Fig. 2. The conversion of 3 was rapid, reaching >99% after 1 h for both RuNPs@SILP-0.33 and RuNPs@SILP-0.66. The least acidic catalyst, RuNPs@SILP-0.33 (Fig. 2a), showed a significant formation of cyclic ether 4 after 1 h, which was gradually converted into alcohol 6 and aliphatic ethers 7 and 8 upon further reaction. In comparison, the more acidic catalyst, RuNPs@SILP-0.66 (Fig. 2b), possessed a much higher activity for the hydrogenolysis of cyclic ether 4 as complete conversion to alcohol 6 and aliphatic ethers 7 and 8 was reached within 5 h. The most acidic catalyst RuNPs@SILP-1.00 (Fig. S13⁺), possessed a similar reaction profile to RuNPs@SILP-0.66, but showed a higher tendency for etherification towards 7 and 8. The distinct reaction profiles illustrate that the quantity of acid sites within RuNPs@SILP have a significant influence on the activity of these bifunctional catalysts.

A series of control experiments were performed to examine the individual role of the two active components forming the bifunctional catalyst for the deoxygenation of **3** (reaction

		Product yield ^{b} (%)						
		Cyclic e	ethers	Alcohol	Aliphatic	e ethers	Alkane	C ₈ -OL yield
SILP Time (h)	Time (h)	4	5	6	7	8	9	(6+7+8)
0.33	16	3	3	42	46	6	0	94
0.66	4	0	2	32	62	3	1	97
1.00	4	0	1	25	66	7	1	98
1.00^{c}	4	1	2	29	66	0	2	95
1.00^{d}	4	5	6	28	60	0	1	88

^{*a*} Reaction conditions: [Ru] (0.016 mmol), SILP (0.5 g), [EMIM]NTf₂ (2.9 mL), substrate (1.6 mmol), H₂ (120 bar), 150 °C. ^{*b*} Conversion >99%, C₈-OL yield = 1-octanol (6) + 1,1-dioctylether (7) + ethyloctylether (8). ^{*c*} 2nd cycle. ^{*d*} 3rd cycle.

conditions: 150 °C, 120 bar $H_{2(g)}$, 4 h). The reaction of substrate 3 over a Ru-free acid catalyst, SILP-1.00 (0.44 mmol), caused the decomposition of 3 into humins. In the presence of a Ru-SILP catalyst without incorporation of the acidic IL 1 (RuNPs@SILP-0.00, 0.016 mmol), no reaction of 3 occurred. The combination of RuNPs@SILP-0.00 (0.016 mmol) with an external acid additive, [1-butyl-3-(4-sulfobutyl)-imidazolium]- NTf_2 (0.44 mmol), provided a system capable of deoxygenating 3 $(C_8$ -OL = 81%); although, the catalytic activity was reduced in comparison to RuNPs@SILP-1.00 (C_8 -OL = 98%) (Table 2). Similar results were also obtained with the combination of commercially available Ru/Al₂O₃ (0.016 mmol) and [1-butyl-3-(4sulfobutyl)-imidazolium]NTf₂ (0.44 mmol) (C_8 -OL = 82%). These results confirm the synergistic interplay of the two active components upon immobilization in the bifunctional catalysts and also the dual role of the SILP to act as both an acid catalyst and stabilizing medium for highly active Ru NPs.

Very high selectivities for the linear C₈-alcohol derivatives corresponding to C8-OL yields of 94-98% could be achieved with all three catalysts (Table 2). The less acidic RuNPs@SILP-0.33 catalyst reached a maximum yield of C8-OLs after 16 h, while RuNPs@SILP-0.66 and RuNPs@SILP-1.00 obtained a maximum C₈-OL yield already after 4 h. The etherification of the primary product 6 towards 7 and 8 increased with an increase in the SILP acidity, but gratifyingly the selectivity for the hydrogenolysis of the secondary over the primary C-O bonds was retained as only small quantities of the over-hydrogenation product ($\leq 3\%$), *n*-octane (9) were observed in all cases. The best catalytic conditions to maximize the C8-OL yield were obtained with RuNPs@SILP-1.00 at 150 °C under 120 bar H_{2(g)} after 4 h in which the total C8-OL yield was 98%. Upon removal of the catalytic products by extraction of the RuNPs@SILP-1.00 with DCM and subsequent extraction of [EMIM]NTf₂ with pentane, the bifunctional catalyst and IL were dried in vacuo for 1 h and re-used in subsequent runs. The principle reactivity profile was well retained with only a slight decrease in activity (C_8 -OL $\geq 88\%$) over three consecutive cycles under these non-optimized recycling conditions.

Catalyst characterization and stability

The structural stability of the bifunctional catalyst was investigated by detailed analysis of the RuNPs@SILP-1.00 material before and after catalysis (Table 3, Fig. 3). BET analysis showed a small increase in the surface area and a decrease in the pore radius for RuNPs@SILP-1.00 after catalysis. This minor change in the textural properties of the bifunctional catalyst likely resulted from the mechanical forces under magnetically stirred conditions. Inductively coupled plasma (ICP) analysis revealed a decrease in the sulfur content of RuNPs@SILP-1.00 during the 1^{st} cycle of catalysis; however, the sulfur content remained constant over the 2^{nd} and 3^{rd} cycles. This finding is consistent with hydrolysis⁶⁴ of weakly bound equivalents of IL 1 from the SiO₂ surface in the 1^{st} cycle.⁶⁵ An accumulation of water within the catalyst system due to the stoichiometric production of water during the deoxygenation of **3** was confirmed by Karl-Fischer titration of the IL phase before catalysis (67 ppm) and after the 3^{rd} catalysis cycle (>650 ppm).

The ICP measurements also demonstrated that the Ru content of the bifunctional catalysts remained constant within experimental error throughout the recycling experiments. High angle annular dark field scanning transmission electron microscopy (HAADF STEM) of RuNPs@SILP-1.00 before catalysis showed the presence of small, well-dispersed Ru NPs (1.7 ± 0.4 nm) (Fig. 3a). After three cycles of catalysis, the Ru NP size remained small (2.1 ± 0.4 nm); however, some of the Ru NPs were observed to aggregate into small clusters (Fig. 3b).

The Ru K-edge X-ray absorption near-edge structure (XANES) spectra of RuNPs@SILP-1.00 showed a similar edge position compared to the reference (Ru foil), which indicated a predominately zero-valent state of the bifunctional catalysts before and after catalysis (Fig. 4a). The Fourier-transformed Ru K-edge extended X-ray absorption fine structure (EXAFS) spectra of RuNPs@SILP-1.00 contained two signals at 1.7 and 2.3 Å (Fig. 4b). The later signal was due to the Ru-Ru scattering of the NPs, while the former signal originated from Ru-O scattering of oxygen stabilizing species on the Ru surface. The spectral simulation, using first-shell Ru-Ru and Ru-O scattering paths, led to good quality fits with the experimental data (see ESI[†] for complete XAS experimental details). In comparison to the reference sample (Ru foil), the heights of the RuNPs@SILP-1.00 signals were much smaller due to the low coordination numbers (CNs) of the Ru NPs. Before catalysis, RuNPs@SILP-1.00 possessed a CN of 4.6, while after the 3rd cycle of catalysis the CN increased to 6.9. After catalysis, an increase in the CN (i.e., EXAFS scattering height)

Table 3 Characterization of RuNPs@SILP-1.00 before and after catalysis

			ICP^{a} (wt%)			
Sample	Surface area $(m^2 g^{-1})$	Pore radius (Å)	Ru	S	Water content of IL phase ^{b} (ppm)	
Before	151	46.3	0.25	4.93	67	
After 1 st cycle	168	40.8	0.23	3.97	_	
After 3 rd cycle	163	41.9	0.26	3.93	>650	

^{*a*} ICP experimental error = $\pm 0.01\%$. ^{*b*} Water content of [EMIM]NTf₂, in the absence of RuNPs@SILP-1.00, as determined by Karl-Fischer titration.



Fig. 3 STEM image (top) and histogram (bottom) of RuNPs@SILP-1.00 (a) before catalysis and (b) after the 3^{rd} catalytic cycle.

showed that some NP growth and aggregation occurred under the catalytic conditions, which was in agreement with the STEM data. However, the CNs for RuNPs@SILP-1.00 were lower than expected for a Ru hcp crystalline structure.66 Direct determination of the NP size using the CNs obtained from EXAFS for the RuNPs@SILP-1.00 samples provided Ru NP sizes < 1 nm,66 which were smaller values than that obtained from the STEM data. As such, the EXAFS analysis offered possible evidence for a bimodal Ru NP population in which the RuNPs@SILP-1.00 samples contain \sim 2 nm Ru NPs (as observed in STEM) and NPs < 1 nm which were not seen in STEM. Lastly, the EXAFS data also showed that the Ru NPs were interacting with an oxygen-based species due to the presence of a Ru-O scattering signal. As the XANES edge position was in agreement with Ru(0) NPs, this data supported the involvement of the surface moieties within SiO2 and/or the sulfonic acid moieties of IL 1 in the stabilization of the Ru NPs.67

Overall, the analytical data confirm the principal stability of the two active components of the RuNPs@SILP material under catalytic conditions. The slight loss of activity during batch-wise recycling (*ca.* 10% over three cycles) may reflect minor changes in the agglomeration of the Ru NPs or accumulation of water within the catalyst system. Thus, using the materials for



Fig. 4 Ru K-edge spectra of the (a) XANES and (b) EXAFS regions for RuNPs@SILP-1.00 before (blue) and after the 3rd catalytic cycle (green) with reference to Ru foil (red).

continuous-flow operation seems an attractive future development.

Optimization of product selectivity for C₈-oxygenates

After assessment of the principal performance of the RuNPs@SILP materials as bifunctional catalysts, we aimed at the selective formation of cyclic ether **4**, alcohol **6** or aliphatic ether **7** as individual products in which the acidity of the SILP and the reaction parameters (*i.e.* temperature, pressure, time, H_2O content) were systematically optimized towards the desired product distribution.

As seen in Fig. 2, the cleavage of the tetrahydrofuran ring within 4 was dependent on the acid loading of the SILP and consequently the lowest acid loaded bifunctional catalyst RuNPs@SILP-0.33 was chosen for optimization of reaction

View Article Online

Chemical Science



Scheme 4 Synthetic pathway for the selective deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (3) toward 2-butyltetrahydrofuran (4), 1-octanol (6) and 1,1-dioctylether (7) using RuNPs@SILP.

temperature and pressure to maximize the yield of 4 (Table S3†). Lowering the reaction temperature from 150 °C to 100 °C dramatically decreased the conversion of substrate 3, while at a medium temperature of 125 °C the deoxygenation rate of 3 remained high while suppressing the hydrogenolysis of the tetrahydrofuran ring (cyclic ether 4 yield = 74%). The H_{2(g)} pressure had a smaller, yet significant influence on the yield of cyclic ether 4, in which decreasing the H_{2(g)} pressure to 80 bar improved the yield of 4 to 83% (Scheme 4). It should be noted that the isomerization of 4 to pyran derivative 5 did not occur to a significant extent under these conditions ($\leq 1\%$) and thus allowed for a high selectivity to cyclic ether 4.

RuNPs@SILP-1.00 was employed as a bifunctional catalyst to obtain selectivity to alcohol **6** since the higher acidity increased the catalytic activity for the hydrogenolysis of cyclic ether **4**. Shifting the product distribution towards the free alcohol **6** was achieved by adding H_2O to the catalyst mixture at the outset of the reaction to prevent the etherification to aliphatic ethers **7** and **8** (Fig. S13†). The simplex algorithm was employed to optimize the parameter set consisting of reaction temperature, time and initial H_2O content towards the maximum yield of alcohol **6** (Table S4†). The results from this optimization are shown in Fig. 5, in which high selectivities toward alcohol **6** stabilized around a series of reaction parameters that provided good yields of alcohol **6** (>55%, >99% conversion of **3**). The optimum conditions were determined to be 150 °C with 0.125 mL H₂O after 16 h to obtain a 1-octanol yield of 60% (Fig. 5, Entry 15). In comparison to the reaction conditions optimized for the total C₈-OL yield (150 °C, 0.00 mL H₂O, 4 h), the selectivity of the product was reversed from the aliphatic ethers (aliphatic ether yield (7 + **8**) = 73%) to the alcohol (alcohol **6** yield = 60%) using this procedure.

Finally, excellent selectivity toward aliphatic ether 7 was achieved using a two-step reaction in which the C₈-OL product mixture obtained using RuNPs@SILP-1.00 under the favoured conditions (150 °C, 0.00 mL H₂O, 4 h; C₈-OL yield: alcohol **6** = 25%, aliphatic ether 7 = 66%) was isolated from the bifunctional catalyst and subsequently reacted as a neat mixture with Nafion® as an acid catalyst.⁶⁸ The mixture of alcohol **6** and aliphatic ether 7 was converted to 95% 7 at 150 °C in 3 h (ref. 69) and the two-step yield from substrate **3** to aliphatic ether 7 was 90%.

The results of this optimization study confirm the flexibility of the catalytic system. The preferred combinations of the catalyst and reaction conditions to synthesize the cyclic ether **4**, the free alcohol **6** or the linear ether **7** are summarized in Scheme **4**.

Synthesis of C₉-oxygenates *via* hydrogenolysis of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10)

A retrosynthetic analysis of 1-nonanol revealed a reaction pathway starting from 5-hydroxymethylfurfural and acetone (Scheme 1). This synthetic scheme involves an aldol condensation of 5-hydroxymethylfurfural and acetone to form 4-(5hydroxymethylfuryl)-2-but-3-en-2-one,⁵⁶ hydrogenation of the aldol condensation adduct to 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10) (see ESI† for synthetic details) and selective deoxygenation of 10 to yield 1-nonanol (13).

The deoxygenation of **10** involves a similar reaction network to substrate **3** (Scheme 5). The removal of the secondary alcohol from **10** leads to the formation of cyclic ethers **11** and **12**. Cleavage of the tetrahydrofuran ring of **11** produces either 1,5or 1,2-nonanediol. Selective deoxygenation of the secondary alcohol moiety within nonanediol provides alcohol **13**. Under



Fig. 5 Optimization of the reaction parameters for the deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (3) using RuNPs@SILP-1.00 (size and colour of data points correspond to the yield of 1-octanol (6)). Reaction conditions: [Ru] (0.016 mmol), SILP-1.00 (0.5 g), total volume = [EMIM]NTf + H₂O (2.9 mL), substrate (1.6 mmol), H₂ (120 bar).



Scheme 5 Reaction network for the deoxygenation of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10) catalyzed by RuNPs@SILPs.



Fig. 6 Optimization of the reaction parameters for the hydrogenolysis of 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10) using RuNPs@SILP-1.00 (size and colour of data points correspond to the yield of 1-nonanol (13)). Reaction conditions: [Ru] (0.016 mmol), SILP-1.00 (0.5 g), total volume = [EMIM]NTf + H₂O (2.9 mL), substrate (1.6 mmol), H₂ (120 bar).

acidic conditions, **13** can undergo etherification to form **1**,1dinonylether (**14**) or ethylnonylether (**15**), while complete deoxygenation of **10** can also occur to form *n*-nonane (**16**). However, the reaction network of substrate **10** differs from substrate **3** in an important point: the primary OH function is already present in the starting material. Thus, the formation of alcohol **13** requires the selective cleavage of three secondary C–O bonds, while retaining a primary C–O bond throughout the reaction.

Based on the experience with the C8-network, RuNPs@SILP-1.00 was chosen as the catalyst material to address this challenge and H₂O was added at the outset of the reaction to favour the formation of the free alcohol 13. The simplex algorithm was employed again to optimize the reaction temperature, time and initial H₂O content to maximum the yield of alcohol 13 (Table S5[†]). The results from this optimization are shown in Fig. 6, in which two areas within the optimization provided good selectivities to alcohol 13 (>50%). The optimum conditions were determined to be 155 $^\circ$ C with 0.090 mL H₂O after 17 h to obtain a free alcohol 13 yield of 57% (Scheme 5, Entry 12) and a total C₉-OL yield of 66% (C₉-OL yield = 1-nonanol (13) + 1,1-dinonylether (14) + ethylnonylether (15)). The remainder of the reaction mixture was composed mainly of the cyclic ethers 11 and 12. Complete deoxygenation of 10 to *n*-nonane (16) was again largely suppressed under these reactions conditions (4%), highlighting again the remarkable selectivity of the bifunctional catalyst for the secondary C-O bond cleavage.

Summary and conclusions

An acid-functionalized imidazolium ionic liquid was covalently attached to SiO_2 to provide a supported ionic liquid phase (SILP) as an acid catalyst and stabilization medium for metal NPs. This SILP material was chosen in the development of bifunctional catalysts to provide a molecular design tool by which the acidity of the support material could be systematically altered. Upon immobilization of Ru NPs from organometallic precursors within the SILPs, bifunctional catalysts were obtained that possessed high catalytic activities, selectivities and recyclabilities in the hydrogenolytic deoxygenation of 4-(2-tetrahydrofuryl)-2-butanol (3) and of 4-(5-(hydroxymethyl)-2tetrahydrofuryl)-2-butanol (10). The higher acid loaded catalysts RuNPs@SILP-0.66 and RuNPs@SILP-1.00 possessed increased catalytic activities, reaching nearly quantitative yields of C8-OL products (1-octanol (6), 1,1-dioctylether (7) and ethyloctylether (8)), in comparison to RuNPs@SILP-0.33. Combined optimization of the SILP acidity and the reaction conditions allowed for a control of the product selectivity to produce 2-butyltetrahydrofuran (4), 1-octanol (6) or 1,1-dioctylether (7) in good to excellent yields (Scheme 4). This opens an attractive and flexible pathway to C8-oxygenates from furfural and acetone as biobased feedstocks. The strategy was extended to the synthesis of the C₉-alcohol 1-nonanol (13) via 5-hydroxymethylfurfural (HMF) as platform chemical. Future studies within our group involve the use of these bifunctional catalysts in the development of continuous-flow processes for the selective deoxygenation of biomass-derived substrates.

Experimental section

Safety warning

High-pressure experiments with compressed $H_{2(g)}$ must be carried out only with appropriate equipment and under rigorous safety precautions.

General

If not otherwise stated, the synthesis of ionic liquids (ILs), supported ionic liquid phases (SILPs) and ruthenium nanoparticles supported on SILPs (RuNPs@SILP) were carried out under an inert atmosphere using standard Schlenk techniques. After synthesis, ILs, SILPs and RuNPs@SILPs were stored under an inert atmosphere. The catalysis substrates 4-(2-tetrahydrofuryl)-2-butanol (3) and 4-(5-(hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10) were stored under atmospheric conditions prior to use. Catalyst solutions and substrates were handled under air, but were flushed with $H_{2(g)}$ prior to catalysis. 4-(2-tetrahydrofuryl)-2-butanol (3),9 4-(5-hydroxymethylfuryl)-2but-3-en-2-one,56 [1-butyl-3-(3-(triethoxysilyl)propyl)imidazolium]Cl,⁷⁰ 3-iodopropyltriethoxy-silane,⁷¹ N-(3-triethoxysilyl) propyl imidazole,⁷¹ 1-(4-sulfobutyl)-3-(3-triethoxysilylpropyl) imidazolium zwitterion,⁴³ [1-butyl-3-(4-sulfobutyl)imidazolium] NTf₂,⁹ [1-butyl-3-methylimidazolium]SO₃(OEt),⁷² [1-butyl-3methylimidazolium]NTf₂ (ref. 73) were synthesized according to known literature methods. SiO₂ (Merck Grade 10184, pore size 100 Å, 63-200 µm) was dehydroxylated in vacuo at 500 °C for at least 16 h prior to use. Anhydrous acetone was prepared by distillation of pre-dried acetone using 4 Å molecular sieves. Toluene and THF were prepared by distillation and drying over activated alumina using a purification system. EtOH (extra dry, absolute) was purchased from Acros Organics. All other chemicals and solvents were purchased from commercial sources and used without purification.

Analytics

Solution-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300, 400 or 600 MHz spectrometer. ¹H and ¹³C NMR spectra were calibrated to TMS using the residual solvent signal. Water content of [EMIM]NTf2 phases was determined using a Metrohm 756 Coulometric Karl-Fischer titrator. ²⁹Si solid-state NMR spectra were obtained using a Bruker AV700 spectrometer. FTIR spectra of the SILP were obtained using a Bruker Alpha spectrometer in the DRIFT mode. Mass spectra (MS) were recorded in positive electrospray mode with a Thermo Scientific LTQ Orbitrap ESI/APCI. Inductively coupled plasma (ICP) was performed at Mikroanalytisches Laboratorium Kolbe (Mülheim an der Ruhr, Germany) on a Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer. High-pressure experiments were performed using in-house engineered 10 and 20 mL stainless steel finger autoclaves. Catalytic reactions were performed in glass inlets using a magnetic stirbar (1000 rpm) and an aluminum heating block. Gas chromatography (GC) was performed on a Thermo Scientific Chromatograph Tace GC Ultra equipped with a CP-WAX-52CB column. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were collected using a Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) operated at 200 kV. Extended X-ray absorption fine structure (EXAFS) spectroscopy was performed on the X18A beamline at the National Synchrotron Light Source (NSLS) in the Brookhaven National Laboratory (NY, USA).

Synthesis of ionic liquids

[1-(4-Sulfobutyl)-3-(3-triethoxysilylpropyl)-imidazolium]NTf₂ (IL 1). 1-(4-Sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium zwitterion43,71 (10.0 g, 24.4 mmol) and bis(trifluoromethane)sulfonimide (7.20 g, 25.6 mmol) were dissolved in anhydrous EtOH (10 mL) and stirred at rt for 1 h. Upon solvent removal, the product was dried in vacuo overnight to yield a viscous amber oil (14.0 g, 83%). ¹H NMR (400 MHz, D_2O): $\delta = 8.77$ (s, 1H, NCHN), 7.48 (m, 2H, NCHCHN), 4.25–4.11 (m, 4H, NCH₂), 3.60 (q, J = 7.1 Hz, 6H, OCH₂), 2.89 (m, 2H, SCH₂), 2.04–1.88 (m, 4H, CH₂), 1.69 (m, 2H, CH_2), 1.15 (t, J = 7.1 Hz, 9H, OCH_2CH_3), 0.57 (m, 2H, SiCH₂). ¹³C NMR (100 MHz, D₂O): δ = 135.2 (s, 1C, NCHN), 122.4 (s, 2C, NCHCHN), 119.9 (q, $J_{CF} = 318$ Hz, 2C, CF₃), 57.4 (s, 3C, OCH₂), 51.6 (s, 1C, NCH₂), 50.0 (s, 1C, NCH₂), 48.9 (s, 1C, SCH₂), 28.0 (s, 1C, CH₂), 23.2 (s, 1C, CH₂), 20.9 (s, 1C, CH₂), 16.7 (s, 3C, OCH₂CH₃), 8.6 (s, 1C, SiCH₂). HRMS/ESI(+) (MeOH) m/z = 395.16669 and 367.13562, calcd for $[C_{15}H_{31}N_2O_6SSi]^+$ = 395.16721 and $[C_{13}H_{27}N_2O_6SSi]^+ = 367.13591$.

[1-Butyl-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ **(IL 2).** 1-Butyl-3-(3-triethoxysilylpropyl)imidazolium chloride⁷⁰ (3.23 g, 8.85 mmol) and bis(trifluoromethane)sulfonimide lithium salt (2.65 g, 9.24 mmol) were dissolved in water (15 mL) and stirred at rt for 10 h. The aqueous phase was extracted with dichloromethane (DCM) (5 × 20 mL) and the combined organic phase was washed with water (3 × 20 mL). The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. The product was dried *in vacuo* to yield a viscous,

colourless liquid (4.86 g, 90%). ¹H NMR (600 MHz, CDCl₃): $\delta =$ ¹³C NMR (150 MHz, CD₃Cl): $\delta =$ 135.4 (s, 1C, NCHN), 122.6 (s, 1C, NCHCHN), 122.5 (s, 1C, NCHCHN), 119.9 (q, $J_{CF} =$ 327 Hz, 2C, CF₃), 58.7 (s, 3C, OCH₂), 52.0 (s, 1C, NCH₂), 50.0 (s, 1C, NCH₂), 32.0 (s, 1C, CH₂), 24.3 (s, 1C, CH₂), 19.4 (s, 1C, CH₂), 18.1 (s, 3C, OCH₂CH₃), 13.2 (s, 1C, CH₃), 7.0 (s, 1C, SiCH₂). HRMS/ ESI(+) (MeOH): m/z = 343.24014 and 329.22501, calcd for [C₁₇H₃₅N₂O₃Si]⁺ = 343.24169 and [C₁₆H₃₃N₂O₃Si]⁺ = 329.22605.

Synthesis of supported ionic liquid phases

SILP-1.00. [1-(4-Sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (6.07 g, 8.80 mmol) was dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO₂ (10.0 g in 50.0 mL toluene). After stirring for 15 min at rt, DCM was removed *in vacuo* and the resulting mixture was refluxed for 18 h. Upon removal of the organic phase, the SILP was washed with DCM (3 × 25 mL) and dried *in vacuo*. The organic phases were combined and solvent removed to determine the residual quantity of IL not grafted onto the dehydroxylated SiO₂ (total IL loading = theoretical loading – recovered residual IL).

SILP-0.66. [1-(4-Sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (4.05 g, 5.87 mmol) and [1-butyl-3-(3-triethoxysilylpropyl)-imidazolium]NTf₂ (1.83 g, 2.93 mmol) were combined and dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO₂ (10.0 g in 50.0 mL toluene). The remainder of the reaction was performed as outline for SILP-1.00.

SILP-0.33. [1-(4-Sulfobutyl)-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (2.02 g, 2.93 mmol) and [1-butyl-3-(3-triethoxysilylpropyl)-imidazolium]NTf₂ (3.66 g, 5.87 mmol) were combined and dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO₂ (10.0 g in 50.0 mL toluene). The remainder of the reaction was performed as outline for SILP-1.00.

SILP-0.00. [1-Butyl-3-(3-triethoxysilylpropyl)imidazolium] NTf₂ (5.49 g, 8.80 mmol) were combined and dissolved in DCM (20 mL) and added to a suspension of dehydroxylated SiO₂ (10.0 g in 50.0 mL toluene). The remainder of the reaction was performed as outline for SILP-1.00.

Synthesis of ruthenium nanoparticles (RuNPs@SILP)

 $[Ru(2-methylally]_2(cod)]$ (5.1 mg, 0.016 mmol) was dissolved in DCM (2 mL) and added to a suspension of SILP (0.5 g in 3 mL of DCM), upon which the SILP changed from a white to a bright yellow colour. The reaction mixture was stirred at rt for 1 h. After solvent removal and *in vacuo* drying of the impregnated SILP, the powder was loaded into a high-pressure autoclave and subjected to an atmosphere of $H_{2(g)}$ (100 bar) at 100 °C for 16 h. Under this reducing environment, the impregnated SILP transformed from a bright yellow to a dark black colour indicating the formation of Ru NPs. Samples were prepared for STEM by mechanical grinding of RuNPs@SILP followed by ultrasound dispersion in acetone. A drop of the obtained suspension was deposited on a copper transmission electron microscopy grid with lacey carbon support film.

Synthesis of catalysis substrates

4-(5-(Hydroxymethyl)-2-tetrahydrofuryl)-2-butanol (10). 5-Hydroxymethylfurfuralacetone (2.98 g, 17.9 mmol) and Ru/C (5 wt%, 125 mg) were combined in a high-pressure reactor. The reaction mixture was heated at 120 °C under an atmosphere of $H_{2(g)}$ (120 bar) for 48 h. The reactor was periodically pressurized with $H_{2(g)}$ to maintain a constant pressure. The reaction mixture was purified over SiO₂ (EtOAc : MeOH, 99:1) to yield a colourless liquid (1.89 g, 61%). ¹H NMR (400 MHz, $CDCl_3$): $\delta = 3.96$ (m, 1H, CHOH), 3.89–3.66 (m, 2H, CH₂OH), 3.62 (ddd, *J* = 5.9, 5.6, 1.7 Hz, 1H, furyl-OCH), 3.43 (ddd, J = 5.9, 5.6, 1.7 Hz, 1H, furyl-OCH), 3.04 (s, 2H, OH), 1.97-1.78 (m, 2H, furyl-CH₂), 1.73-1.63 (m, 1H, furyl-CH₂), 1.63-1.54 (m, 2H, butyl-CH2 and furyl-CH2), 1.54-1.39 (m, 3H, butyl-CH₂), 1.12 (d, J = 6.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 80.1$ (dd, furyl-OCH), 77.2 (t, furyl-OCH), 67.8 (d, CHOH), 65.0 (d, CH₂OH), 36.0 (d, butyl-CH₂), 32.1 (d, butyl-CH₂), 31.5 (d, furyl-CH₂), 27.0 (d, furyl-CH₂), 23.5 (d, CH₃). HRMS/ESI(+) (MeOH with MeCO₂H): m/z = 197.11478, calcd for $[C_9H_{18}O_3Na]^+ = 197.11482$.

Deoxygenation of biomass substrates

Hydrogenolysis of 4-(2-tetrahydrofuryl)-2-butanol. In a typical experiment, RuNPs@SILP (0.5 g), [EMIM]NTf₂ (2.9 mL) and 3 (231 mg, 1.6 mmol) were combined in a glass insert and placed in a high-pressure autoclave. After purging the autoclave with $H_{2(g)}$, the reaction mixture was stirred at 150 °C in an aluminum heating block under 120 bar H_{2(g)} for 4 h. Once the reaction was finished, the reactor was cooled in an ice bath, carefully vented and the RuNPs@SILP was extracted with DCM (3×5 mL). Upon removal of the solvent, the IL phase was extracted with pentane (3 \times 8 mL), the organic phase was dried over MgSO4 and the solvent was evaporated. The product was obtained as a colourless liquid and analyzed via GC using tetradecane as an internal standard. For recyclability experiments, RuNPs@SILP-1.00 and [EMIM]NTf₂ were recombined after product extraction with the aid of DCM (1 mL). Upon drying of the catalyst mixture in vacuo at rt for at least 1 h, 3 (231 mg, 1.6 mmol) was added and the reaction mixture was stirred at 150 °C under 120 bar $H_{2(g)}$ for 4 h.

Hydrogenolysis of 4-(5-(hydroxymethyl)tetrahydro-2-furyl)-2butanol. In a typical experiment, RuNPs@SILP (0.5 g), [EMIM] NTf₂ + H₂O (2.9 mL) and 10 (279 mg, 1.6 mmol) were combined in a glass insert and placed in a high-pressure autoclave. After purging the autoclave with H_{2(g)}, the reaction mixture was stirred at the desired temperature in an aluminum heating block under 120 bar H_{2(g)}. Once the reaction was finished, the reactor was cooled in an ice bath, carefully vented and the RuNPs@SILP was extracted with DCM (3 × 5 mL). Upon removal of the solvent, the IL phase was extracted with pentane (3 × 8 mL), the organic phase was dried over MgSO₄ and the solvent was evaporated. The product was obtained as a colourless liquid and analyzed *via* GC using tetradecane as an internal standard.

Acknowledgements

This work was performed as a part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative of the German federal and state government to promote science and research at German universities. The authors would like to thank Karl-Josef Vaeßen (ITMC, RWTH Aachen University) for $N_{2(g)}$ adsorption measurements, as well as Dr Markus Hölscher (ITMC, RWTH Aachen University) and Dr Nils Theyssen (Max-Planck-Institut für Kohlenforschung) for their generous support. Use of the X18A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract no. DE-AC02-98CH10886. Center for Functional Nanomaterials at BNL is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract no. DE-AC02-98CH10886. KLL would also like to thank Deutscher Akademischer Austaush Dienst (DAAD) for financial support.

Notes and references

- 1 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
- 2 M. Stocker, Angew. Chem., Int. Ed., 2008, 47, 9200-9211.
- 3 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- 4 M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547.
- 5 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev.*, 2014, 114, 1827–1870.
- 6 J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183.
- 7 T. Werpy and G. Peterson, *Top Value Added Chemicals from Biomass*, 2004.
- 8 F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2010, **49**, 5510–5514.
- 9 J. Julis and W. Leitner, *Angew. Chem., Int. Ed.*, 2012, **51**, 8615–8619.
- 10 T. vom Stein, J. Klankermayer and W. Leitner, in *Catalysis for the Conversion of Biomass and its Derivatives*, ed. M. Behrens and A. K. Datye, epubli, Berlin, Germany, 2013, pp. 411–434.
- 11 A. J. Janssen, F. W. Kremer, J. H. Baron, M. Muether, S. Pischinger and J. Klankermayer, *Energy Fuels*, 2011, 25, 4734–4744.
- 12 W. Leitner and J. Julis, World Pat., WO 2013/144315 A1, 2013.
- 13 Medium chain alcohols can in principle be produced from the reduction of medium chain fatty acids obtained from coconut or palm kernel oil; although, the natural abundance of caprylic (C_8) and capric (C_{10}) acid are low ($\leq 6\%$ of the total fatty acid compostion) K. Bunyakiat, S. Makmee, R. Sawangkeaw and S. Ngamprasertsith, *Energy Fuels*, 2006, **20**, 812–817.
- 14 W. K. R. Dittmeyer, G. Kreysa and A. Oberholz, *Winnacker-Küchler: Chemische Technik*, Wiley-VCH, Weinheim, 2003–2005.

- - 16 B. Heuser, T. Laible, M. Jakob, F. Kremer and S. Pischinger, SAE [Tech. Pap.], 2014, DOI: 10.4271/2014-01-1253.
 - 17 T. G. Liu and C. Khosla, Annu. Rev. Genet., 2010, 44, 53-69.
 - 18 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
 - 19 A. D. Sutton, F. D. Waldie, R. L. Wu, M. Schlaf, L. A. Silks and J. C. Gordon, *Nat. Chem.*, 2013, 5, 428–432.
 - 20 W. J. Xu, Q. N. Xia, Y. Zhang, Y. Guo, Y. Q. Wang and G. Z. Lu, *ChemSusChem*, 2011, **4**, 1758–1761.
 - 21 R. M. West, Z. Y. Liu, M. Peter and J. A. Dumesic, *ChemSusChem*, 2008, 1, 417–424.
 - 22 R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, G. P. van Walsum, H. Pendse and G. W. Huber, *Green Chem.*, 2010, 12, 1933–1946.
 - 23 J. F. Yang, N. Li, G. Y. Li, W. T. Wang, A. Q. Wang, X. D. Wang, Y. Cong and T. Zhang, *ChemSusChem*, 2013, 6, 1149–1152.
 - 24 Z. Li, R. S. Assary, A. C. Atesin, L. A. Curtiss and T. J. Marks, *J. Am. Chem. Soc.*, 2014, **136**, 104–107.
 - 25 R. Alamillo, M. Tucker, M. Chia, Y. Pagan-Torres and J. Dumesic, *Green Chem.*, 2012, **14**, 1413–1419.
 - 26 W. J. Xu, H. F. Wang, X. H. Liu, J. W. Ren, Y. Q. Wang and G. Z. Lu, *Chem. Commun.*, 2011, 47, 3924–3926.
 - 27 S. Koso, I. Furikado, A. Shimao, T. Miyazawa, K. Kunimori and K. Tomishige, *Chem. Commun.*, 2009, 2035–2037.
 - 28 T. Buntara, S. Noel, P. H. Phua, I. Melian-Cabrera, J. G. de Vries and H. J. Heeres, *Angew. Chem., Int. Ed.*, 2011, **50**, 7083–7087.
 - 29 J. Jae, W. Q. Zheng, R. F. Lobo and D. G. Vlachos, *ChemSusChem*, 2013, **6**, 1158–1162.
 - 30 Y. Nakagawa, H. Nakazawa, H. Watanabe and K. Tomishige, *ChemCatChem*, 2012, **4**, 1791–1797.
 - 31 M. Chia, Y. J. Pagan-Torres, D. Hibbitts, Q. H. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis and J. A. Dumesic, *J. Am. Chem. Soc.*, 2011, 133, 12675– 12689.
 - 32 J. Lee, Y. T. Kim and G. W. Huber, *Green Chem.*, 2014, **16**, 708–718.
 - 33 M. Schlaf, Dalton Trans., 2006, 4645-4653.
 - 34 C. P. Mehnert, E. J. Mozeleski and R. A. Cook, *Chem. Commun.*, 2002, 3010–3011.
 - 35 A. Riisager, K. M. Eriksen, P. Wasserscheid and R. Fehrmann, *Catal. Lett.*, 2003, **90**, 149–153.
 - 36 A. Riisager, P. Wasserscheid, R. van Hal and R. Fehrmann, *J. Catal.*, 2003, **219**, 452–455.
 - 37 M. H. Valkenberg, C. deCastro and W. F. Holderich, *Green Chem.*, 2002, 4, 88–93.
 - 38 C. P. Mehnert, R. A. Cook, N. C. Dispenziere and M. Afeworki, J. Am. Chem. Soc., 2002, 124, 12932–12933.
 - 39 U. Hintermair, G. Franciò and W. Leitner, *Chem.-Eur. J.*, 2013, **19**, 4538-4547.
 - 40 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis and R. D. Rogers, *Chem. Commun.*, 2001, 135–136.

- 41 P. Li, L. Wang, Y. Zhang and G. Wang, *Tetrahedron*, 2008, **64**, 7633–7638.
- 42 A. S. Amarasekara and O. S. Owereh, *Catal. Commun.*, 2010, **11**, 1072.
- 43 Q. A. Zhang, J. Luo and Y. Y. Wei, *Green Chem.*, 2010, **12**, 2246–2254.
- 44 Y. Gu, C. Ogawa, J. Kobayashi, Y. Mori and S. Kobayashi, Angew. Chem., Int. Ed., 2006, 45, 7217–7220.
- 45 H. H. Zhao, N. Y. Yu, Y. Ding, R. Tan, C. Liu, D. H. Yin,
 H. Y. Qiu and D. L. Yin, *Microporous Mesoporous Mater.*,
 2010, 136, 10–17.
- 46 X. L. Zhang, D. F. Wang, N. Zhao, A. S. N. Al-Arifi, T. Aouak,
 Z. A. Al-Othman, W. Wei and Y. H. Sun, *Catal. Commun.*,
 2009, 11, 43–46.
- 47 Y. Kume, K. Qiao, D. Tomida and C. Yokoyama, *Catal. Commun.*, 2008, **9**, 369–375.
- 48 L. Luza, A. Gual, D. Eberhardt, S. R. Teixeira, S. S. X. Chiaro and J. Dupont, *ChemCatChem*, 2013, 5, 2471–2478.
- 49 M. A. Gelesky, S. S. X. Chiaro, F. A. Pavan, J. H. Z. dos Santos and J. Dupont, *Dalton Trans.*, 2007, 5549–5553.
- 50 S. Miao, Z. Liu, B. Han, J. Huang, Z. Sun, J. Zhang and T. Jiang, *Angew. Chem., Int. Ed.*, 2006, **45**, 266–269.
- 51 J. Huang, T. Jiang, H. Gao, B. Han, Z. Liu, W. Wu, Y. Chang and G. Zhao, *Angew. Chem., Int. Ed.*, 2004, 43, 1397–1399.
- 52 H. Hagiwara, T. Nakamura, T. Hoshi and T. Suzuki, *Green Chem.*, 2011, **13**, 1133–1137.
- 53 J. Dupont and J. D. Scholten, *Chem. Soc. Rev.*, 2010, **39**, 1780–1804.
- 54 N. Yan, C. X. Xiao and Y. Kou, *Coord. Chem. Rev.*, 2010, **254**, 1179–1218.
- 55 K. L. Luska and A. Moores, *ChemCatChem*, 2012, 4, 1534–1546.
- 56 J. Julis, M. Hölscher and W. Leitner, *Green Chem.*, 2010, 12, 1634–1639.
- 57 K. L. Luska and A. Moores, *Adv. Synth. Catal.*, 2011, 353, 3167–3177.
- 58 K. L. Luska and A. Moores, *Green Chem.*, 2012, **14**, 1736–1742.
- 59 S. Winterle and M. A. Liauw, *Chem. Ing. Tech.*, 2010, **82**, 1211–1214.
- 60 N. Yan, Y. A. Yuan, R. Dykeman, Y. A. Kou and P. J. Dyson, Angew. Chem., Int. Ed., 2010, 49, 5549–5553.
- 61 L. Han, S. W. Park and D. W. Park, *Energy Environ. Sci.*, 2009, 2, 1286–1292.
- M. Pursch, R. Brindle, A. Ellwanger, L. C. Sander, C. M. Bell,
 H. Handel and K. Albert, *Solid State Nucl. Magn. Reson.*, 1997,
 9, 191–201.
- 63 Theoretical Ru loading = 0.32%. Discrepancy between theoretical and experimental Ru loading likely resulted from an incomplete removal of organic impurities (ex. dichloromethane, cyclooctane) introduced during the Ru NP synthesis.
- 64 W. Long and C. W. Jones, ACS Catal., 2011, 1, 674-681.
- 65 Desulfonation of RuNPs@SILP-1.00 could also account for the decreased sulfur content; however, this mechanism did not fit with our data as a continuous lose of sulfur would be expected in subsequent catalytic cycles.

- 66 A. M. Beale and B. M. Weckhuysen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5562–5574.
- 67 The possible formation of Ru oxide could not be ruled out. XPS analyses of RuNPs@SILP-1.00 were inconclusive due to the low metal loading of these samples.
- 68 G. A. Olah, T. Shamma and G. K. S. Prakash, *Catal. Lett.*, 1997, 46, 1-4.
- 69 Reaction conditions (similar to ref. 65): 1-octanol (2.17 mL, 13.7 mmol), 1,1-dioctylether (10.9 mL, 36.3 mmol) and Nafion (1.0 g) were combined together and heated at 150

°C for 3 h. The product mixture was analyzed by GC using tetradecane as internal standard.

- 70 K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G. A. Park and
 D. W. Park, *Green Chem.*, 2012, 14, 2933–2940.
- 71 M. Lombardo, S. Easwar, A. De Marco, F. Pasi and C. Trombini, *Org. Biomol. Chem.*, 2008, **6**, 4224–4229.
- J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, *Green Chem.*, 2002, 4, 407–413.
- 73 H. Uchimura and M. Kikuta, EP Pat., EP1707265 A1, 2006.