Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 1411

www.rsc.org/greenchem

PAPER

Simple and recyclable ionic liquid based system for the selective decomposition of formic acid to hydrogen and carbon dioxide†‡

M. E. M. Berger,[a] D. Assenbaum,[a] N. Taccardi,[a] E. Spiecker[b] and P. Wasserscheid*[a]

Received 19th November 2010, Accepted 4th February 2011
DOI: 10.1039/c0gc00829j

Exploitation of hydrogen as an energy carrier requires the development of systems for its storage and delivery. Formic acid has been proposed as valuable hydrogen carrier compound, due to its relatively high hydrogen content (53 g L^{-1}), the latter being easily and cleanly released in catalytic reactions under mild conditions ($HCOOH \rightarrow H_2 + CO_2$). Ionic liquids are interesting solvents for homogeneous catalyzed formic acid decomposition systems as their extremely low volatility avoids solvent contamination of the produced hydrogen stream. In this paper an outstandingly simple, robust and active catalyst system is presented, namely $RuCl_3$ dissolved in 1-ethyl-2,3-dimethylimidazolium acetate ($RuCl_3$/[EMMIM][OAc]). This system proved to be fully recyclable over 10 times. Turnover frequencies (TOF) of 150 h^{-1} and 850 h^{-1} were obtained at 80 °C and 120 °C, respectively.

Introduction

Concerns about global warming and depletion of the fossil hydrocarbons motivate the development of more sustainable solutions for the problem of energy supply. In this context, the use of hydrogen as an energy carrier is believed to play a growing role in the future.[1] However, the advent of the so-called *hydrogen economy* requires fixing the problem of hydrogen storage, transport and distribution. One of the technical concepts under discussion is to chemically bind hydrogen in liquid *energy carrier* compounds. A suitable energy carrier compound should provide high hydrogen content, easy and clean hydrogen release and favourable physicochemical properties.

Formic acid (FA) has been proposed as an attractive hydrogen carrier substance.[2] FA contains 4.4 w/w% of hydrogen, resulting in a storage density of 53 g hydrogen per litre. The use of FA as an energy carrier molecule is based on a cycle where hydrogen generated from a renewable energy source, *e.g.* photovoltaic driven electrolysis, is converted to FA, *via* CO_2-hydrogenation. The yielded FA can be transported and distributed. In event of an energy consumption peaks, FA can be catalytically decomposed on demand to regenerate hydrogen and CO_2 ($HCOOH \rightarrow H_2 + CO_2$).[3] The re-hydrogenation of CO_2 closes the cycle and makes it carbon-neutral and sustainable.[4]

Pioneering works by Laurenczy *et al.* have shown that a clean and efficient FA decomposition can be achieved in aqueous solutions using a water-soluble Ru-phosphine catalyst at 120 °C.[5] The authors were able to recycle the catalyst solution and realised a reaction system for the continuous release of hydrogen at high pressure. In another important contribution, Beller and co-workers showed the feasibility of the decomposition of the azeotrope formed by FA with some tertiary amines.[6] They developed a catalytic system that showed remarkable activity already at 40 °C and atmospheric pressure. While this work was in preparation, Deng and co-workers published the use of ionic liquids (ILs) as the reaction media for FA decomposition.[7] Ionic Liquids are a class of saline compounds with melting points below 100 °C. With respect to applications in catalysis, ionic liquids have been shown to offer unique combinations of properties, such as *e.g.* negligible low vapour pressure and tuneable polarity, solubility and miscibility properties.[8] Deng *et al.* suggested the use of amino-functionalised ILs to fix some of the problems dealing with the formerly proposed FA decomposition methods, namely the need of relatively high temperature in the case of aqueous system (Laurenczy *et al.*[5]) and the amine contaminated hydrogen product in the case of the azeotropic system (Beller *et al.*[6]). Their work indeed demonstrated the clean decomposition of FA at 60 °C at atmospheric pressure. However, the authors state clearly that they were not able to recycle the catalyst solution.

In this contribution, we present a detailed study demonstrating that for IL-based FA decomposition systems, the catalyst

---

[a] *Chemical Reaction Engineering, Department of Chemical and Bioengineering, Egerlandstrasse 3, Erlangen, 91058, Germany*
[b] *Center for Nanoanalysis and Electron Microscopy, Department of Material Science, Cauerstr. 6, 91058 Erlangen, Germany*

† Electronic supplementary information (ESI) available: Table of all experiments and further experimental information. See DOI: 10.1039/c0gc00829j

‡ This paper was published as part of the themed issue of contributions from the Green Solvents – Alternative Fluids in Science and Application conference held in Berchtesgaden, October 2010.

Table 1 Decomposition of FA in ILs: anion variation

Entry	Ionic liquid	FA conversion [%][a]	Out-gas composition[b]			Yield H_2 (%)
			(H_2) [%]	(CO_2) [%]	(CO) [%]	
1	[EMIM][PF_6][c]	25.8	5.2	4.0	9.6	9.1
2	[EMIM][OTf]	9.1	6.8	4.9	0.0	9.1
3	[EMIM][$N(CN)_2$]	10.3	2.9	9.2	3.9	4.3
4	[EMIM][$EtSO_4$]	11.0	7.2	5.2	0.5	10.2
5	[EMIM][$OctSO_4$]	93.9	31.1	25.3	0.4	92.7
6	[EMIM][$MeP(OMe)O_2$]	73.0	28.6	22.1	0.4	71.9
7	[EMIM][$HP(OMe)O_2$]	67.8	25.5	19.5	2.5	61.7
8	[EMIM][NTf_2]	71.0	32.5	25.8	0.0	71.0
9	[EMIM][OAc]	59.1	27.2	16.4	0.0	59.1
10	[EMMIM][OAc]	91.1	32.1	25.3	0.0	91.1

Reaction conditions: ionic liquid 3.0 g, $RuCl_3$ 2.1 mg (10.1 μmol), sodium formate 68.0 mg (1.0 mmol), formic acid 0.46 g (10.0 mmol), reaction time 84 h, temperature 80 °C.[a] Estimated from product gas composition. [b] The N_2 added in the beginning complementary to 100%. [c] **Caution**: formation of HF.

performance and recyclability depends strongly on the nature of the IL anion. Moreover, we propose a new, efficient and very robust IL-based FA decomposition system that is simply formed by a non-functionalized ionic liquids and $RuCl_3$ as catalyst precursor.

Results and discussion

Firstly, the influence of the ionic liquid anion on the FA decomposition activity of a homogeneously dissolved Ru-compound was investigated. As 1-ethyl-3-methylimidazolium ([EMIM]) ionic liquids possess favourable physicochemical properties (*e.g.* low viscosity, high thermal stability, wide liquid range),[9] we performed the anion screening using ionic liquids with this cation. To test the more basic acetate anion, the cation 1-ethyl-2,3-dimethylimidazolium (EMMIM) was also used. In fact, it is known that 1,3-dialklyimidazolium salts have the tendency to form N-heterocyclic carbenes (NHC) in the presence of basic anions.[10] Therefore, by comparing the results of [EMIM] and [EMMIM] cations, it would have been possible to investigate the potential influence of *in situ* formed NHC. Concerning the Ru-source in the screening experiments, we selected the simple $RuCl_3$ as catalyst precursor, in absence of any ligand or stabilizer.

All reactions were carried out in a pressurised vessel applying 12 bar of nitrogen gas as an inert protecting atmosphere. The reaction progress was monitored by measuring the pressure increase due to the formation of CO_2 and hydrogen, followed by GC analyses of the resulting gas mixtures. The results obtained by varying the anions are shown in Table 1.

The results of entries 1–4 clearly showed that the $[EMIM]^+$ salts of $[PF_6]^-$, $[OTf]^-$, $[N(CN)_2]^-$ and $[EtSO_4]^-$ anions were unsuitable as reaction solvents for the FA decomposition reaction. In these ionic media only conversions below 30% were observed over the 84 h reaction time. Moreover, the product gas composition of these unreactive $RuCl_3$/ionic liquid systems showed a strong variability depending on the nature of the IL anion. While the reaction in [EMIM][OTf] (entry 2 in Table 1) produced no detectable CO, the reaction in [EMIM][PF_6], [EMIM][$N(CN)_2$] and [EMIM][$EtSO_4$] resulted in significant amounts of CO in the product gas. In the case of hexafluorophosphate melt, CO was even found to be the main reaction product, being the CO concentration significantly higher than that of CO_2 in the gaseous phase. (**caution**: in using the ionic liquid [EMIM][PF_6], massive corrosion of the used autoclave was observed. This indicated the formation of HF when the FA decomposition was carried out under the applied conditions).

It is worth noting, that FA decomposition in [EMIM][$EtSO_4$] and [EMIM][$OctSO_4$] produced in both cases very similar amounts of CO (5100 ppm *vs.* 4000 ppm, respectively; see entries 4 and 5) but a sharp difference in the reactivity was observed for these two structurally similar media (FA conversion 11.0% *vs.* 93.9%, respectively). It could be hypothesised that the different steric demands of the two alkylsulfate ions resulted in the formation of different catalytically active species from the catalyst precursor $RuCl_3$ (see further in the text).

For all other anions used in these screening experiments (entries 6–10), the FA conversion ranged between 59% and 94%, confirming that FA decomposition was feasible in a variety of different ILs using solely $RuCl_3$ as the catalyst precursor. However, among the more effective IL/catalyst solutions, there were systems yielding significant amounts of CO: 4400 ppm of CO were detected in the product gas of the reaction in [EMIM][$MePO_2(OMe)$] while 25 400 ppm of CO were produced in [EMIM][$HPO_2(OMe)$]. Clearly, in the context of hydrogen storage technologies, these levels of by-produced CO are unacceptable in pursuing a clean and ready applicable FA decomposition process. As matter of fact, the presence of CO would require a much more complicated downstream gas purification procedure if the produced gas should be applied, for instance, in a fuel cell device.[11] Accordingly, our screening experiments allowed us to identify three ionic liquid candidates as the most promising, as they combined good reactivity with ideal selectivity, namely: [EMIM][NTf_2], [EMIM][OAc] and [EMMIM][OAc]. Using these ionic liquid media, the only detectable gaseous products of the FA decomposition were hydrogen and CO_2. The deviation from the expected molar ratio of 1 : 1 was due to the known fact that CO_2 shows a significantly higher solubility in the ionic liquid than hydrogen.[12] Thus, the lower CO_2 observed in the gas phase was attributed to the dissolution of part of the produced CO_2 in the IL phase. Comparing the reactivity in the two acetate melts, it was clear

Table 2 Recycling runs in FA decomposition using repetitive batch mode experiment with two different $RuCl_3$/IL reaction systems

			Out-gas composition[b]			
Entry	Ionic liquid	FA conversion [%][a]	(H_2) [%]	(CO_2) [%]	(CO) [%]	Yield H_2 (%)
1.1	[EMIM][NTf_2]	71.0	32.5	25.8	0.0	71.0
1.2	[EMIM][NTf_2]	4.9	4.1	3.5	0.0	4.9
2.1	[EMMIM][OAc]	91.1	32.1	25.3	0.0	91.1
2.2	[EMMIM][OAc]	99.9	34.2	26.0	0.0	99.9
	⋮					
2.10	[EMMIM][OAc]	99.9	33.2	26.0	0.0	99.9

Reaction conditions: ionic liquid 3.00 g, $RuCl_3$ 2.1 mg (10.1 μmol), sodium formate 68.0 mg (1.0 mmol), addition of 0.5 g formic acid each run; reaction time 22–70 h, temperature 80 °C.[a] Estimated from product gas composition. [b] The N_2 added in the beginning complementary to 100%.

that the catalyst in [EMIM][OAc] was significantly less active than in [EMMIM][OAc]. This suggested a likely *in situ* NHC complex formation, leading to a decreased catalytic activity.

Following these anion variation experiments, we focused our attention in finding out whether the two promising catalytic systems $RuCl_3$/[EMIM][NTf_2] and $RuCl_3$/[EMMIM][OAc] would allow repetitive utilization for hydrogen production from FA. In order to demonstrate this very important practical aspect, recyclability tests were performed by depressurizing the reactor after a first FA decomposition run and re-charging it with fresh FA. Interestingly, the addition of FA to the ionic liquid phase always caused a vigorous effervescence. As stated previously, this was in accordance to the fact that CO_2 partly dissolved in the ionic liquid phase. The addition of fresh FA to the ionic liquid caused a drastic fall of pH, affecting the solubility of CO_2, which was released to a great extent. After adding the new charge of FA, the reactors were closed, pressurized with nitrogen and heated to the reaction temperature. The results of the recycling experiments are listed in Table 2. For sake of brevity and clarity the results of the recycling runs 2.3–2.9 were omitted. However, the standard deviations of the mean conversion and hydrogen yield over the whole recycling series did not exceed ±5.6%, indicating very stable catalytic performance. In none of the experiments, CO was detectable in the gaseous products.

In full agreement with earlier work by Deng and co-workers[7] on similar systems, the $RuCl_3$/[EMIM][NTf_2] ionic catalyst solution was found to lose almost completely its activity right after the first run. In contrast, the $RuCl_3$/[EMMIM][OAc] system resulted to be very robust and selective, yielding stable performance over 10 runs. Remarkably, the catalytic system showed a significantly long activation phase in the first run which disappeared in the run thereafter. Such an induction period was clearly indicating the slow formation of the active catalytic species for FA decomposition from the $RuCl_3$ precursor. In this regard, the comparison of the pressure/time profiles of the FA decomposition reactions would be more instructive than the simple analysis of the gas phase product after 84 h reaction time. Fig. 1 shows the reaction profiles of the initial run and the first, the fifth and the ninth recycle. While in the initial run a clear induction time was observed during the first 10 h of experiment, the recycles did not show such an activation period. Moreover, the initial reaction was still incomplete even after 50 h reaction time, while all recycling runs showed an almost superimposable pressure/time profile and full conversion of FA in less than 20 h.

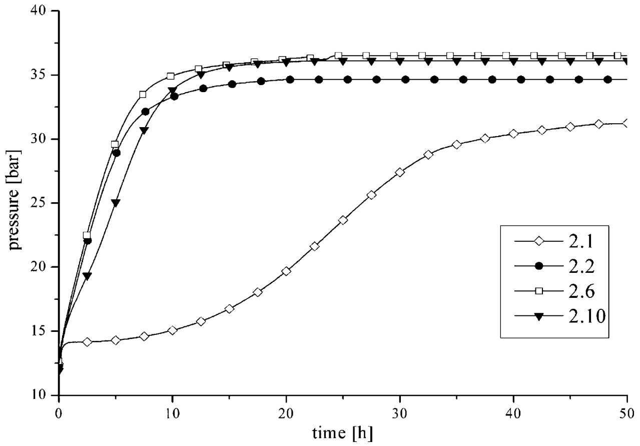

Fig. 1 Pressure/time-profiles for the catalytic FA decomposition in the $RuCl_3$/[EMMIM][OAc] system.

No significant sign of deactivation was observed from the first recycling run (2.2) to the ninth recycling run (2.10).

In a second set of recycling experiments with the [EMMIM][OAc]/$RuCl_3$ system, we investigated the effect of reaction temperature on reaction rate and selectivity. Once the catalyst had reached steady performance after 3 recycles, the temperature was varied from 60 °C up to 120 °C in four additional recycles. A final recycle at 80 °C confirmed the stability of the reaction system under all applied reaction conditions. The results of the temperature variation experiments are listed in Table 3 and the corresponding pressure/time profiles are depicted in Fig. 2.

Interestingly, there is a significant step in activity between the reaction temperatures of 60 °C and 80 °C. Different reasons may account for this observation. However, it is reasonable to assume this temperature dependency related to the energy needed to form the active catalytic species in the applied reaction system. Comparing the catalytic activities obtained with the here presented $RuCl_3$/[EMMIM][OAc] system to the recently published[5] $RuCl_3$/TPPTS in water, our phosphane ligand free catalyst proved to be somewhat more active (TOF for $RuCl_3$/[EMMIM][OAc] = 280 h^{-1} *vs.* 210 h^{-1} for $RuCl_3$/TPPTS in water[5]).

Finally, two mechanistic aspects were addressed in our study, namely the origin of the observed induction period and the

Table 3 FA decomposition in the catalytic system $RuCl_3$/[EMMIM][OAc]: effect of reaction temperature

			Out-gas composition[b]				
Entry	Reaction T/°C	FA conversion [%][a]	(H_2) [%]	(CO_2) [%]	(CO) [%]	Yield H_2 (%)	TOF (mol H_2/mol Ru h)
1	60	23.0	19.7	17.7	0.0	23.0	20
2	80	99.9	33.9	27.3	0.0	99.9	150
3	100	100.0	35.2	30.0	0.0	100.0	280
4	120	100.0	34.8	27.6	0.0	100.0	850

Reaction conditions: ionic liquid [EMMIM][OAc] 3.00 g, $RuCl_3$ 2.1 mg (10.1 μmol), sodium formate 68.0 mg (1.0 mmol), formic acid 0.5 g (10.9 mmol), reaction time 20 h;[a] Estimated from product gas composition; [b] N_2 complementary to 100%.

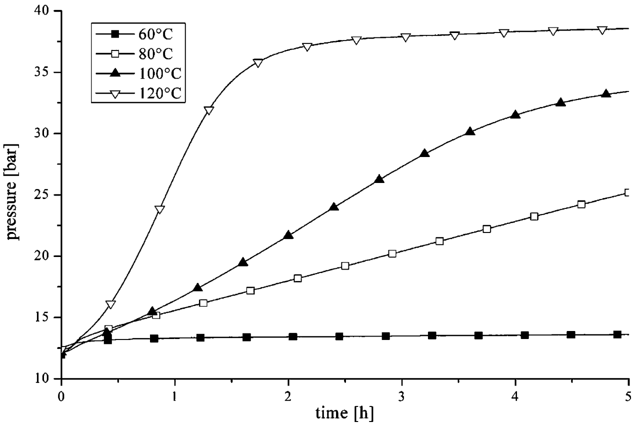

Fig. 2 Reaction profile pressure *vs.* time for $RuCl_3$ catalysed FA decomposition in [EMMIM][OAc] at different temperatures.

remarkable difference in recyclability between the $RuCl_3$ catalyst system in [EMMIM][OAc] *vs.* [EMIM][NTf_2].

Concerning the observed induction period, such catalyst behaviour was already observed by Laurenczy and co-workers[5] These authors suggested a reduction process of their Ru(III) catalyst precursor to the Ru(II) active catalyst species triggered by the added formiate. In order to check this hypothesis for our system we studied Ru-precursors in different oxidation states in the ionic liquid [EMMIM][OAc]. The resulting pressure/time profiles are depicted in Fig. 3.

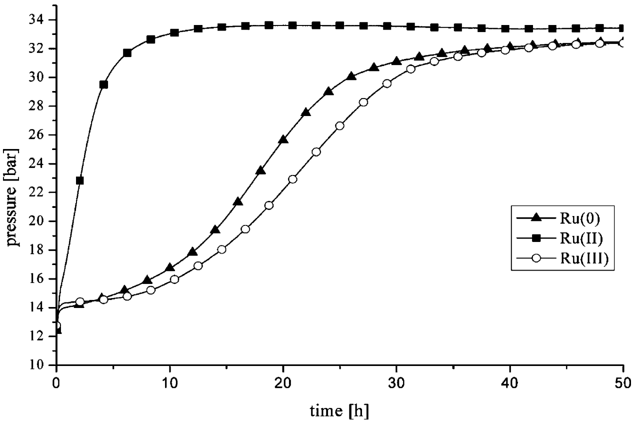

Fig. 3 Reaction profile pressure *vs.* time for Ru catalysed FA decomposition in [EMMIM][OAc] using catalyst precursor of different Ru oxidation states.

Clearly, no induction time was observed when the reaction was carried out in presence of Ru(II) complex [(*p*-cymene)$RuCl_2$]$_2$ in the ionic liquid [EMMIM][OAc]. Interestingly, both the Ru(III) and the Ru(0) pre-catalyst showed a similar induction phase. This strongly supported the assumption of a Ru(II) complex being the active species in the FA decomposition reaction. In case of Ru(III) complexes the pre-reduction was required, on the other hand the Ru(0) precursor was pre-oxidized to form the most active catalytic species.

A closer look to the remarkable difference of the $RuCl_3$/[EMIM][NTf_2] *vs.* the $RuCl_3$/[EMIM][OAc] system with respect to catalyst recycling was taken, by investigating the ionic catalyst solutions after the first FA decomposition run with transmission electron microscopy (TEM, for details of the measurements see Supporting Information†). While in the acetate melt no hint for Ru particle formation was found, the TEM picture of the NTf_2 melt showed clearly the presence of Ru nanoparticles of 3–5 nm diameter (Fig. 4a). To clarify whether the formation of these nano-colloidal Ru species is responsible for the observed deactivation, an additional experiment was carried out. Ru nanoparticles of 3–5 nm size were independently synthesised through thermolysis of Ru_3CO_{12} in [EMIM][NTf_2] (Fig. 4b). This solution was then tested for catalytic activity in FA decomposition under identical conditions to the previous catalytic experiments. As a result, only a very sluggish reaction was observed (5% conversion after 24 h). Remarkably, the data obtained in this test with the *ex situ* prepared nano-colloidal Ru in [EMIM][NTf_2] were perfectly comparable to the performance of the recycled $RuCl_3$/[EMIM][NTf_2] solution (Table 2, entry 1.2).

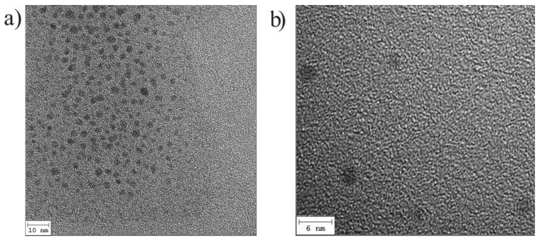

Fig. 4 a) Ru nano-particles observed after the first run in FA decomposition using $RuCl_3$/[EMIM][NTf_2] as the catalyst system; b) Nano-colloidal Ru synthesised through thermolysis of Ru_3CO_{12} in [EMIM][NTf_2].

Further evidence of the active catalyst species in FA decomposition being indeed a homogeneous Ru(II) complex dissolved in the ionic liquid could be obtained through Hg poisoning experiments. The catalytic performance of the $RuCl_3$/[EMMIM][OAc] system remained unaffected when the reaction was performed in presence of Hg (see Supporting Information for details†). Moreover, the outcome of the TEM analysis and Hg poisoning experiments were also indirectly corroborated by the strong influence of different ionic liquid anions on the catalytic performance (see Table 1). The latter, indeed, could well be understood when taking into account a homogeneous catalytic species with the ionic liquid anion acting as a more or less coordinating part in the Ru(II) complex ligand sphere.

Conclusion

In this study, we identified and investigated an outstanding simple, active and recyclable ionic liquid based system for the catalytic decomposition of formic acid. The most efficient system, $RuCl_3$ dissolved in [EMMIM][OAc], was shown to produce hydrogen and carbon dioxide as the only products and was recyclable for at least nine recycle runs. During these recycles no sign of deactivation or change in selectivity was observed.

Based on the anion variation study, TEM measurements, Hg poisoning experiments and catalytic runs with different Ru catalyst precursors we conclude that the active catalyst in the ionic liquid is an homogeneously dissolved Ru(II) complex with the ionic liquid taking part in the stabilization of the metal centre. It is worth noting that this simple catalytic system formed solely of $RuCl_3$ dissolved in [EMMIM][OAc] exhibits very attractive catalytic activity with turnover frequencies of 150 h^{-1} at 80 °C and 850 h^{-1} at 120 °C.

Experimental

Unless otherwise stated, all reagents and catalysts were commercial and used as received. With the exception of [EMMIM][OAc] and [EMIM][OAc], all used ionic liquids tested were commercial and used as received. The gas-analysis was done with a Varian 450 GC equipped with a Restek Shincarbon ST 100/120 column. The NMR spectra were recorded on a Jeol ECX 400 spectrometer.

Synthesis of [EMMIM][OAc] and [EMIM][OAc]

A 100 g scale synthesis of these ILs was performed as follows: glacial acetic acid (1 eq.) was added drop-wise to a solution of the relevant alkylimidazolium methylcarbonate in methanol at 0 °C. The resulting solution was transferred to a rotavapor and the solvent evaporated. The final liquid was dried overnight at 50 °C in high vacuum. The compounds identity was confirmed by NMR in D_2O.

General reaction procedure

The reactions were carried out in steel autoclaves with a glass inlet and a total volume of 28 mL. The ionic liquid (3.0 g), formic acid (0.46 g), sodium formate (0.068 g) and the catalyst (10.1 µmol ruthenium) were charged into the reactor. The system was purged with nitrogen and then pressurized to 12 bar. Then, the reactor was placed in a heating block and heated at the desired temperature. The reaction progress was monitored by a digital manometer. Conversion and TOF were calculated from the pressure values and the GC analysis data (knowing the total reactor volume, and using the ideal gas law). For the recycling experiments, after cooling and venting, formic acid (0.50 g) was added to the reaction mixture. Then the reactor was newly purged with nitrogen and finally pressurized with 12 bar of nitrogen. The reaction was re-started by switching on the heating.

Acknowledgements

The authors like to thank the Deutsche Forschungsgemeinschaft (DFG) that has provided through its Erlangen Excellence Cluster "Engineering of Advanced Materials" significant support for this project. M. B. acknowledges support by the Erlangen Graduate School of Molecular Science.

References

1 (*a*) F. H. Sobrino, C. R. Monroy and J. L. H. Perez, *Renewable Sustainable Energy Rev.*, 2010, **14**(2), 772–780; (*b*) D. G. Vlachos and S. Caratzoulas, *Chem. Eng. Sci.*, 2010, **65**(1), 18–29; (*c*) Y. H. P. Zhang, *Energy Environ. Sci.*, 2009, **2**, 272–282; (*d*) N. Z. Muradov and T. N. Veziroglu, *Int. J. Hydrogen Energy*, 2008, **33**(23), 6804–6839.
2 F. Joó, *ChemSusChem*, 2008, **1**, 805–808.
3 Y. Himeda, *Green Chem.*, 2009, **11**, 2018–2022.
4 (*a*) P. G. Jessop, *Handbook of Homogeneous Hydrogenation* Wiley-VCH 2007, 489–511; (*b*) S. Schulien, G. Sandstede and W. H. Hahn, *Int. J. Hydrogen Energy*, 1999, **24**, 299–303.
5 C. Fellay, N. Yan, P. J. Dyson and G. Laurenczy, *Chem.–Eur. J.*, 2009, **15**, 3752–3760.
6 A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem*, 2008, **1**(8–9), 751–758.
7 X. Li, X. Ma, F. Shi and Y. Deng, *ChemSusChem*, 2010, **3**(1), 71–74.
8 (*a*) V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**(6), 2615–2665; (*b*) P. Wasserscheid, P. S. Schulz in *Ionic Liquids in Synthesis*, ed. P. Wasserscheid, T. Welton, 2nd edition, Wiley-VCH, 2007, 369–463; (*c*) T. Welton, *Coord. Chem. Rev.*, 2004, **248**, 2459–2477.
9 S. Werner, M. Haumann and P. Wasserscheid, *Annu. Rev. Chem. Biomol. Eng.*, 2010, **1**, 203–230.
10 (*a*) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445–3478; (*b*) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687–703.
11 E. J. Granite and T. O'Brien, *Fuel Process. Technol.*, 2005, **86**, 1423–1434.
12 (*a*) B. Wittich and U. K. Deiters, *J. Phys. Chem. B*, 2010, **114**, 8954–8960; (*b*) S. Raeissi and C. J. Peters, *Green Chem.*, 2009, **11**, 185–192; (*c*) A. Finotello, J. E. Bara, D. Camper and R. D. Noble, *Ind. Eng. Chem. Res.*, 2008, **47**(10), 3453–3459.