

COMMUNICATION



New metal extractants and super-acidic ionic liquids derived from sulfamic acid†

Cite this: *Chem. Commun.*, 2016, 52, 7032

David Dupont, Evelien Renders, Stijn Raiguel and Koen Binnemans*

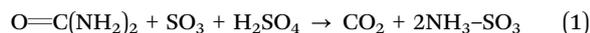
Received 17th March 2016,
Accepted 4th May 2016

DOI: 10.1039/c6cc02350a

www.rsc.org/chemcomm

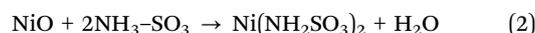
Sulfamic acid (NH₂–SO₃) is an acidic zwitterion with many applications. *N*-Alkylated derivatives are introduced, which can be used as a new class of metal extractants R₂NH–SO₃ and as new super-acidic ionic liquids [R₂NH–SO₃H][Tf₂N]. The synthesis, properties and novel applications of this versatile platform are discussed.

Sulfamic acid is an interesting compound due to its zwitterionic nature and relatively strong acidity (p*K*_a ≈ 1).¹ It is closely related to sulfuric acid, but it is a solid, making it unique among the strong inorganic acids. It is prepared industrially by reacting urea with sulfur trioxide and sulfuric acid (eqn (1)).^{2,3}



Sulfamic acid is best described by the formula ⁺NH₃–SO₃[–] and not by the tautomeric form NH₂–SO₃H, since the equilibrium is almost completely shifted in the direction of the zwitterion.^{1–4} It is used in a wide variety of applications such as household cleaning products because it is a safe, non-toxic alternative to the more volatile and corrosive hydrochloric acid. Furthermore, its ability to form soluble metal complexes with metal ions such as Ca(II) and Fe(III), makes it very efficient for the removal of limescale and rust.^{2,3} Sulfamic acid is also used in herbicides and flame retardants in the form of ammonium sulfamate.^{2,3} Furthermore, *N*-alkylated sulfamic acid derivatives have been of great interest as artificial sweeteners (*e.g.* sodium cyclamate) and as therapeutic compounds in antibiotics, HIV inhibitors and anti-cancer drugs.^{1–3,5,6} The synthesis and chemistry of *N*-alkylated sulfamate derivatives has been reviewed by Benson *et al.* (1980).¹ Recently, interest has also grown in the domain of green chemistry and acid catalysis since (*N*-alkylated) sulfamic acids are considered to be eco-friendly, reusable and versatile acid catalysts.^{7–12} Metal sulfamate salts and complexes are also

of interest because of their very high solubility, due to the zwitterionic nature of sulfamic acid.¹ In fact, many sulfamate salts are amongst the most soluble metal salts known (*e.g.* Ni²⁺, Pb²⁺), making it an ideal counterion for high current density electroplating.^{2,3,13} Metal sulfamates can be prepared by reaction between sulfamic acid and a metal carbonate or oxide (eqn (2)):



Sulfamate ions are ambivalent ligands, which leads to a rich coordination chemistry.¹ For example, sulfamate complexes of Zn(II), Co(II), Ni(II) and rare-earth ions (La–Lu, Y) are bonded through the oxygen atom, while sulfamate complexes of Pt(II), Pt(IV), Cr(III), and Ru(III) are bonded through the nitrogen atom.^{1,14–18} The strong affinity for metal ions and the differences in coordination behaviour suggest that *N*-alkylated sulfamic acid derivatives (p*K*_a ≈ –2)¹ could be excellent extractants. However, to the best of our knowledge, such extractants have not been reported yet. This communication focuses on the extraction of metal ions with new *N*-alkylated (zwitterionic) sulfamic acid extractants (R₂NH–SO₃), but also introduces closely-related double protonated *N*-alkylated sulfamic acid ionic liquids ([R₂NH–SO₃H][Tf₂N]) (Fig. 1), as an interesting new class of super acids (p*K*_a < –7) which are more convenient and safer to handle than current super acids (*e.g.* FSO₃H). These super-acidic ionic liquids can serve as new non-aqueous metal leaching systems.

The synthesis of *N*-alkylated sulfamic acids is straightforward, using mono- or dialkylamines and chlorosulfonic acid



Fig. 1 Synthesis of *N*-alkylated sulfamic acid zwitterions R₂NH–SO₃ and the corresponding super-acidic (double protonated) ionic liquids [R₂NH–SO₃H][Tf₂N].

KU Leuven, Department of Chemistry, Celestijnenlaan 200F – P.O. Box 2404, B-3001 Heverlee, Belgium. E-mail: Koen.Binnemans@chem.kuleuven.be

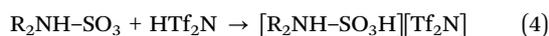
† Electronic supplementary information (ESI) available: List of used chemicals, equipment, synthesis procedures and characterization data. See DOI: 10.1039/c6cc02350a

Table 1 List of the zwitterion extractants R_2NH-SO_3 and the corresponding protonated ionic liquids $[R_2NH-SO_3H][Tf_2N]$ described in this work

| Nr | Compound | T_m^a (°C) |
|----|------------------------------|--------------------------|
| 1 | $(Et)_2NH-SO_3$ | Decomposes around 250 °C |
| 2 | $(n-Oct)_2NH-SO_3$ | Decomposes around 250 °C |
| 3 | $[(Et)_2NH-SO_3H][Tf_2N]$ | 59 |
| 4 | $[(n-Oct)_2NH-SO_3H][Tf_2N]$ | 63 |

^a Melting temperature (T_m): measured by DSC.

to obtain the corresponding *N*-alkylated sulfamic acid (eqn (3)).¹ Trialkylamines can not be used as these form stable non-acidic adducts with SO_3 instead of the sulfamic acid derivative.¹⁹ The resulting *N*-alkylated sulfamic acid zwitterions are moderately strong acids ($pK_a \approx 2$),¹ but they can also undergo an additional protonation in the presence of very strong Brønsted acids, to form ionic liquids (eqn (4)).¹ Bistriflimic acid (HTf_2N) was used in this work since Tf_2N^- anions tend to form thermally stable, low-melting and lowly-viscous ionic liquids.²⁰



An overview of the synthesis procedures can be found in the ESI.† A list of the synthesized compounds is given in Table 1 and their miscibility with various solvents is summarized in Table 2.

The thermal stability of these compounds was investigated in detail. In a first series of experiments these compounds were tested at 25, 50 and 80 °C in water over a period of 24 h, during which no signals of degradation were detected by NMR (ESI,† Tables S2 and S3). Thermogravimetric analysis (TGA) under nitrogen atmosphere (5 °C min⁻¹) showed no degradation below 250–350 °C (Fig. 2). The TGA results are also compared with analogous sulfonic acid and alkylsulfuric acid ionic liquids.^{21,22}

Compounds **1** and **2** were then tested as extractants (15 mol% in the organic phase) in a series of solvent extraction experiments using a biphasic water/heptane mixture (1 : 1 vol/vol) and a metal concentration of 1 mmol L⁻¹ (pH 2.7) in the aqueous phase. The samples were shaken for 1 h at 25 °C, and then allowed to phase separate. Total reflection X-ray fluorescence (TXRF) was used to

Table 2 Miscibility of the *N*-alkylated sulfamic acid derivatives (**1–4**) in different solvents (1 : 1 ratio vol/vol)^a

| | 1 | 2 | 3 | 4 |
|-------------------------------|---|---|---|---|
| Water | + | – | – | – |
| Ethylene glycol | – | – | + | + |
| Acetonitrile | + | – | + | – |
| <i>N,N</i> -Dimethylformamide | + | + | – | – |
| Methanol | + | + | + | + |
| Ethanol | + | + | + | + |
| Acetone | + | + | + | + |
| Toluene | – | ± | – | ± |
| <i>n</i> -Heptane | – | ± | – | – |

^a Miscible (+), partially miscible (±) or immiscible (–).

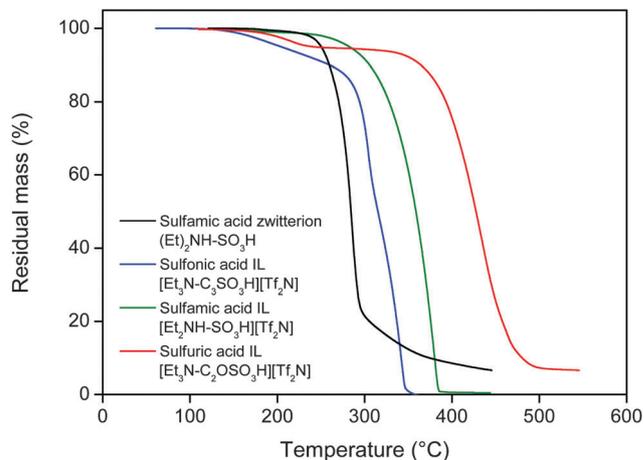


Fig. 2 TGA results (5 °C min⁻¹) for the sulfamic acid zwitterion $(Et)_2NH-SO_3H$ and the corresponding IL $[(Et)_2NH-SO_3H][Tf_2N]$. The TGA curves of the analogue sulfonic acid IL $[(Et)_3N-C_3SO_3H][Tf_2N]$ and alkylsulfuric acid IL $[(Et)_3N-C_2OSO_3H][Tf_2N]$ are added as a comparison and were obtained in previous work.^{21,22}

measure the metal concentrations in the aqueous and organic phase in order to calculate the percentage extraction %*E* (eqn (5)):

$$\%E = \frac{n_{org}}{n_{org} + n_{aq}} \quad (5)$$

Here, n_{org} and n_{aq} are the number of moles of the metal ion in the organic phase and aqueous phase, respectively. The influence of the extractant structure and the choice of metal counter ion (chloride or nitrate) was tested (Fig. 3). The extractant $(Et)_2NH-SO_3$ performs significantly better in extraction than its homologue $(Oct)_2NH-SO_3$ with longer alkyl chains. There is also a noticeable increase in extraction efficiency from nitrate media compared to chloride media. Very little is known about this type of sulfamic acid extractants. Therefore, we are currently conducting further research to elucidate the extraction mechanism using EXAFS measurements. Overall, these alkylated sulfamic acids appear to be interesting extractants, especially for the extraction of metal ions from nitrate solutions. Advantages of this new class

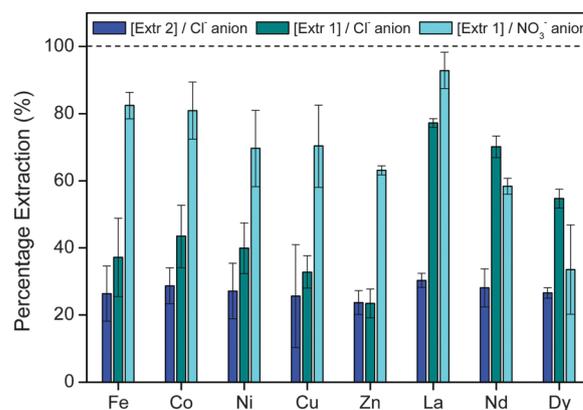


Fig. 3 Influence of the counter ions (chloride, nitrate) and the extractant structure (Extr 1 $(Et)_2NH-SO_3$ or Extr 2 $(Oct)_2NH-SO_3$) on the percentage extraction (%*E*) of the ions: Fe(III), Co(II), Ni(II), Cu(II), Zn(II), La(III), Nd(III), Dy(III).

of extractants are that they show no detergent behaviour and that they are less acidic ($pK_a \approx 2$) than sulfonic acids ($R-SO_3H$) which have a $pK_a \approx -2$ and show strong detergent behaviour.^{21,23,24} The higher pK_a of sulfamic acids makes it easier to strip the metals from the extractants, while retaining the typical behaviour of $-SO_3H$ extractants.^{21,25} It is also interesting that a reversed extraction trend is present for the lanthanide ions, similarly to what was observed for the closely related sulfonic acid and alkylsulfuric acid extractants.^{21,22}

The sulfamic acid based ionic liquids (compound **3** and **4**) are also interesting new Brønsted-acid ILs. To the best of our knowledge, no examples of such protonated sulfamic acid ILs have been reported until now. Existing reports claiming to have synthesized ILs such as $[Et_3N-SO_3H][Cl]$,²⁶ and $[butylimidazolium-SO_3H][Cl]$,²⁷ are strongly in contradiction with the well-established knowledge of sulfamation chemistry since tertiary amines do not undergo sulfonation when contacted with chlorosulfonic acid (eqn (3)), instead forming non-acidic adducts $R_3N \cdot SO_3$.^{1,19} Sulfamic acid ILs described in earlier reports, such as $[succinimide-SO_3H][HSO_4]$,²⁸ may in fact be in equilibrium with H_2SO_4 and succinimide- SO_3 . It has been shown that the corresponding acid (H_2SO_4 $pK_a \approx -3$) is unable to fully protonate the sulfamic acid group thus resulting in cross-protonation.¹ The complete protonation of sulfamic acid, required to form an ionic liquid, can only be achieved using super acids since literature data showed that even $HClO_4$ is unable to fully protonate sulfamic acid.¹ We therefore selected the super acid bistriflimic acid (HTf_2N).²⁹ The resulting compounds $[R_2NH-SO_3H][Tf_2N]$ had a melting point around $60^\circ C$ (Table 2) and can therefore be considered as an ionic liquid ($T_m < 100^\circ C$). Their acidity was tested qualitatively in chloroform to avoid the levelling effect of water. Equimolar amounts of phenol were added to compare the degree of protonation of phenol (^{13}C NMR) with other strong mineral acids: H_2SO_4 ($pK_{a1} \approx -3$) and HSO_3Cl which is an even stronger acid than $HClO_4$ ($pK_a \approx -10$).³⁰⁻³² The full experimental procedure is given in the ESI.† Compounds **3** and **4** as well as HSO_3Cl were able to fully protonate phenol ($pK_a = -7$),³³ while H_2SO_4 resulted only in the partial protonation of phenol.³²

This result shows in a qualitative way that these ILs are super acidic ($pK_a < -7$), but further NMR studies will be carried out to measure the exact acidity constant.^{31,32} The interest of these super-acidic ILs resides in the fact that they represent non-volatile and stable super acids, which are miscible in organic solvents and solid at room temperature, making them convenient to handle and to store. They are therefore safe to use, especially compared to other super acids, which are usually volatile fluorinated or chlorinated liquids at room temperature and much more dangerous to handle (e.g. FSO_3H , CF_3SO_3H).³⁴⁻³⁶ Using these ILs, diluted in $[C_2mim][Cl]$ (1-ethyl-3-methylimidazolium chloride) (1:1 wt/wt), we were able to efficiently dissolve high concentrations of metal oxides such as CuO , NiO , ZnO , MnO , MnO_2 , Co_3O_4 , Fe_2O_3 , La_2O_3 , Nd_2O_3 , and Dy_2O_3 . The strong acidity of the sulfamic acid IL, combined with the solvating ability of the chloride ions in $[C_2mim][Cl]$ makes this non-aqueous system efficient for the dissolution of metal oxides. This non-aqueous leaching system can be operated up to $200^\circ C$

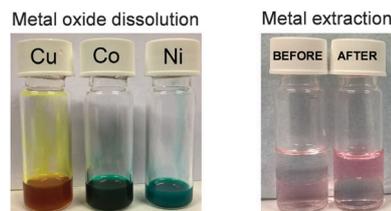


Fig. 4 NiO , CuO and Co_3O_4 dissolved in $[(Et)_2NH-SO_3H][Tf_2N] : [C_2mim][Cl]$ 1:1 wt/wt (left). Extraction of $Co(II)$ ions from an aqueous chloride solution to a *n*-heptane phase containing the zwitterion extractant $(Et)_2NH-SO_3$ (right).

(no decomposition was observed), which greatly enhances the dissolution kinetics. A visualisation of the metal oxide dissolution in sulfamic acid ILs and the previously discussed solvent extraction of metal ions is provided in Fig. 4.

To demonstrate the strength of this leaching system, we show the dissolution of the notoriously inert lamp phosphors $LaPO_4 \cdot Ce^{3+}, Tb^{3+}$ (LAP) and $BaMgAl_{10}O_{17}$ (BAM). These compounds are very relevant to the recycling of rare earths from lamp phosphor waste but current state-of-the-art recycling methods still use energy-intensive alkali fusion ($700-1000^\circ C$ with Na_2CO_3) to convert them into simple oxides so that they can be further processed.³⁷⁻³⁹ Fig. 5 shows the influence of the sulfamic acid IL/ $[C_2mim][Cl]$ ratio on the dissolution of BAM and LAP, demonstrating a clear synergy. The dissolution kinetics were also studied as function of the temperature (90 , 150 and $200^\circ C$), and show a significant increase in dissolution speed (ESI,† Fig. S1). We tested other IL diluents but $[C_2mim][Cl]$ showed by far the best performance (ESI,† Fig. S2).

Finally, it is also worth mentioning that in the past acidic ILs (e.g. sulfonic acids) have been used as acid catalysts for organic reactions.^{36,40-48} The super-acidic ILs described in this work could therefore be of interest to researchers in this field as they show a broad miscibility with organic solvents (Table 2).^{21,42}

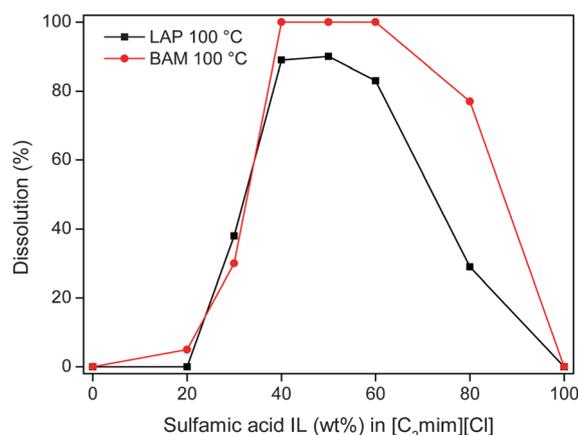


Fig. 5 Dissolution of the lamp phosphors $BaMgAl_{10}O_{17} \cdot Eu^{2+}$ (BAM) and $LaPO_4 \cdot Ce^{3+}, Tb^{3+}$ (LAP) using different mixtures of $[C_2mim][Cl]$ and $[(Et)_2NH-SO_3H][Tf_2N]$. The mixture was stirred at $100^\circ C$ for 24 h (solid/liquid ratio: 1/200).

In summary, we have synthesized different *N*-alkylated sulfamic acid zwitterions ${}^+NR_2H-SO_3^-$ and the corresponding protonated sulfamic acid ILs $[NR_2H-SO_3H][Tf_2N]$. *N*-Alkylated sulfamic acid zwitterions are introduced as a promising new class of acidic metal extractants with a convenient acidity ($pK_a \approx 2$) and easy synthesis. The corresponding protonated sulfamic acid ILs are new super strong acids, which are safer to handle than currently known super acids (e.g. FSO_3H , CF_3SO_3H) which are often volatile and/or unstable. The use of super-acidic sulfamic acid ILs dissolved in $[C_2mim][Cl]$ resulted in a strong leaching system, capable of dissolving very inert metal compounds in a temperature range of 25–200 °C. Further research on metal processing and recycling with these promising ILs is ongoing. This communication intends to introduce these new compounds derived from sulfamic acid and show some of its potential applications in the field of metal processing.

The authors wish to thank the KU Leuven (projects GOA/13/008 and IOF-KP RARE³) and the FWO Flanders (PhD fellowship to DD) for financial support.

Notes and references

- 1 G. A. Benson and W. J. Spillane, *Chem. Rev.*, 1980, **80**, 151–186.
- 2 A. Metzger, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.
- 3 K. Yoshikubo and M. Suzuki, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., Oxford, 2000.
- 4 R. L. Sass, *Acta Crystallogr.*, 1960, **13**, 320–324.
- 5 J.-Y. Winum, A. Scozzafava, J.-L. Montero and C. T. Supuran, *Med. Res. Rev.*, 2005, **25**, 186–228.
- 6 W. Spillane and J.-B. Malaubier, *Chem. Rev.*, 2014, **114**, 2507–2586.
- 7 Z. Li, X. Ren, P. Wei, H. Wan, Y. Shi and P. Ouyang, *Green Chem.*, 2006, **8**, 433–436.
- 8 A. Santra, G. Guchhait and A. K. Misra, *Green Chem.*, 2011, **13**, 1345–1351.
- 9 B. Wang, Y. Gu, L. Yang, J. Suo and O. Kenichi, *Catal. Lett.*, 2004, **96**, 71–74.
- 10 M. Zarghani and B. Akhlaghinia, *RSC Adv.*, 2015, **5**, 87769–87780.
- 11 F. Shirini and N. G. Khaligh, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2011, **186**, 2156–2165.
- 12 F. Shirini and N. G. Khaligh, *Dyes Pigm.*, 2012, **95**, 789–794.
- 13 R. C. Barret, *Plating*, 1954, **41**, 1027–1033.
- 14 M. S. Wickleder and A. Mietrach, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2089.
- 15 M. N. Hughes, J. R. Lusty and T. J. Barton, *J. Chem. Soc., Dalton Trans.*, 1975, 1478–1483.
- 16 M. S. Wickleder, *Chem. Rev.*, 2002, **102**, 2011–2088.
- 17 M. S. Wickleder, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1794–1798.
- 18 M. S. Wickleder, *J. Alloys Compd.*, 2000, **303–304**, 445–453.
- 19 R. J. W. Cremllyn, *Chlorosulfonic Acid*, Royal Society of Chemistry, Cambridge, UK, 2002.
- 20 J. D. Holbrey, R. D. Rogers, R. A. Mantz, P. C. Trulove, V. A. Cocalia, A. E. Visser, J. L. Anderson, J. L. Anthony, J. F. Brennecke, E. J. Maginn, T. Welton and R. A. Mantz, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2008, pp. 57–174.
- 21 D. Dupont, S. Raiguel and K. Binnemans, *Chem. Commun.*, 2015, **51**, 9006–9009.
- 22 D. Dupont, E. Renders and K. Binnemans, *Chem. Commun.*, 2016, **52**, 4640–4643.
- 23 G. Y. Markovits and G. R. Choppin, in *Ion Exch. Solvent Extr.*, ed. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, USA, 1973, vol. 3, pp. 51–81.
- 24 E. O. Otu and A. D. Westland, *Solvent Extr. Ion Exch.*, 1991, **9**, 875–883.
- 25 T. C. Lo, M. H. I. Baird and C. Hanson, *Handbook of solvent extraction*, Wiley-Interscience, New York, 1983.
- 26 A. Zare, A. R. Moosavi-Zare, M. Merajoddin, M. A. Zolfigol, T. Hekmat-Zadeh, A. Hasaninejad, A. Khazaei, M. Mokhlesi, V. Khakyzadeh, F. Derakhshan-Panah, M. H. Beyzavi, E. Rostami, A. Arghoon and R. Roohandeh, *J. Mol. Liq.*, 2012, **167**, 69–77.
- 27 M. Ghorbani, S. Noura, M. Oftadeh, M. Narimani and K. Behbodi, *J. Mol. Liq.*, 2015, **209**, 224–232.
- 28 M. Abedini, F. Shirini and J. M.-A. Omran, *J. Mol. Liq.*, 2015, **212**, 405–412.
- 29 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2002.
- 30 S. Li, F. Tao and R. Gu, *Sci. China, Ser. B: Chem.*, 2008, **51**, 305–315.
- 31 S. Brownstein and A. E. Stillman, *J. Phys. Chem.*, 1959, **63**, 2061–2062.
- 32 A. Koeberg-Telder, H. J. A. Lambrechts and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 293–298.
- 33 D. R. Dalton, *Foundations of Organic Chemistry: Unity and Diversity of Structures, Pathways, and Reactions*, Wiley, Hoboken, 2011.
- 34 D. Himmel, S. K. Goll, I. Leito and I. Krossing, *Angew. Chem., Int. Ed.*, 2010, **49**, 6885–6888.
- 35 R. D. Howells and J. D. Mc Cown, *Chem. Rev.*, 1977, **77**, 69–92.
- 36 G. Olah, O. Farooq, A. Husain, N. Ding, N. Trivedi and J. Olah, *Catal. Lett.*, 1991, **10**, 239–247.
- 37 K. Binnemans and P. T. Jones, *J. Rare Earths*, 2014, **32**, 195–200.
- 38 K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton and M. Buchert, *J. Cleaner Prod.*, 2013, **51**, 1–22.
- 39 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856–868.
- 40 M. Röper, E. Gehrler, T. Narbeshuber and W. Siegel, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, 2000.
- 41 G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, 1968, **90**, 2726–2727.
- 42 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.*, 2002, **124**, 5962–5963.
- 43 D. Fang, X.-L. Zhou, Z.-W. Ye and Z.-L. Liu, *Ind. Eng. Chem. Res.*, 2006, **45**, 7982–7984.
- 44 M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, Z. Asgari, V. Khakyzadeh and A. Hasaninejad, *J. Ind. Eng. Chem.*, 2013, **19**, 721–726.
- 45 J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu and Z. Sun, *Catal. Commun.*, 2004, **5**, 473–477.
- 46 P. N. Muskawar, S. Senthil Kumar and P. R. Bhagat, *J. Mol. Catal. A: Chem.*, 2013, **380**, 112–117.
- 47 D.-J. Tao, J. Wu, Z.-Z. Wang, Z.-H. Lu, Z. Yang and X.-S. Chen, *RSC Adv.*, 2014, **4**, 1–7.
- 48 C. Yue, D. Fang, L. Liu and T.-F. Yi, *J. Mol. Liq.*, 2011, **163**, 99–121.