Effects of acidity and immiscibility of lactam-based Brønsted-acidic ionic liquids on their catalytic performance for esterification[†]

Hancheng Zhou, Jing Yang, Linmin Ye, Haiqiang Lin and Youzhu Yuan*

Received 12th October 2009, Accepted 20th January 2010 First published as an Advance Article on the web 19th February 2010 DOI: 10.1039/b921081d

Several lactam-based Brønsted-acidic ionic liquids with different acidities were synthesized and applied to the esterification of carboxylic acids with alcohols. High conversion and perfect selectivity were obtained under mild conditions. Among the ionic liquids investigated, those having a methyl sulfonate anion (which has weaker acidity than those with a tetrafluoroborate anion) afforded the highest activity for esterification. The results indicated that the acidity and immiscibility of Brønsted-acidic ionic liquids has a synergistic effect on their esterification performance. Furthermore, after removal of water under vacuum, such ionic liquids could be reused several times without substantial loss of activity.

Introduction

Many organic esters, ranging from aliphatic to aromatic, are produced in high volume for their extensive application in pharmaceuticals, agrochemicals, foods and fine chemicals.¹ They are mainly manufactured by the fundamental esterification reaction. However, esterification, which was formerly catalyzed by inorganic acids, e.g. sulfuric acid,² faced the unavoidable problems of deactivation of catalyst,3 side reaction and corrosion of equipment and tedious isolation of catalyst-product. To overcome the drawbacks caused by homogeneous catalysts, a number of other catalyst systems such as resins,⁴ supported mineral acids,5 heteropoly acids,6 and zeolites7 have been developed. These catalysts, due to the tendency to deactivation, operation loss, and high transfer resistance, could not be used in large-scale production.8 Therefore, the development of a highly efficient, easily separable catalyst system for the esterification of carboxylic acid with alcohol is still highly desired.

Room-temperature ionic liquids (ILs), owing to their negligible volatility, selective solubility and tunable structures,⁹⁻¹¹ have been successfully applied in several classical organic reactions.¹²⁻¹⁵ Protic ionic liquids are an interesting subset of ILs. One of the key properties of such ILs is that the proton transfer from the acid to the base leads to the presence of proton-donor and -acceptor sites, which can be used to build up a hydrogen-bonded network.^{16,17} Efficient esterification can be obtained by use of ILs, specifically protic Brønsted-acidic ILs,¹⁸⁻²⁴ such as 1-butyl-3-methylimidazolium *para*toluenesulfonicacid ([BMIm][PTSA]),¹⁸ 1-methylimidazolium tetrafluoroborate ([HMIm][BF₄]),¹⁹

zolium hydrosulfate ([BMIm][HSO₄]),²⁰ N-propanesulfonic acid pyridinium tetrafluoroborate ([PSPy][BF₄]),²¹ N-methyl-2-pyrrolidonium methyl sulfonate ([NMP][CH₃SO₃]),²² triphenyl(propyl-3-sulfonyl)phosphonium para-toluenesulfonate ([Ph₃P(CH₂)₃SO₃H][PTSA]),^{23,24} etc. The catalytic activities varied considerably depending on the properties of ILs. For instance, a satisfactory yield for the esterification of acetic acid and 1-butanol was obtained with both [HMIm][BF4] and [NMP][CH₃SO₃], but the catalyst [NMP][CH₃SO₃] showed higher activity.^{19,22} In the case of using [HMIm][BF₄] as a catalyst, very high yields could be achieved when the volume of the IL catalyst was equal to carboxylic acid and the reaction temperature was as high as 110 °C.19 In the case of [NMP][CH₃SO₃], however, the reaction proceeded smoothly by using a molar ratio of IL catalyst to substrate of 25% based on carboxylic acid (used throughout this investigation) at room temperature.²² In order to better understand the essence of such difference and to construct better Brønsted-acidic ILs for esterification, it is necessary to explore the effect of acidity and immiscibility of Brønsted-acidic ILs on their catalytic performance.

In this work, *N*-methyl-2-pyrrolidone (NMP) and caprolactam (CP) were chosen as precursors to synthesize lactam-based Brønsted-acidic ILs with different Hammett acidity function (H_0) (Scheme 1). The results showed that the acidity and immiscibility of such lactam-based Brønsted-acidic ILs had a synergistic effect on their esterification performance.



X=BF₄, NO₃, CH₃SO₃, TFA

Scheme 1 The synthesis of lactam-based Brønsted-acidic ILs.

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China. E-mail: yzyuan@xmu.edu.cn; Fax: +86 592-2183047; Tel: +86 592-2181659

[†] Electronic supplementary information (ESI) available: NMR, TG-DTA, acidity, UV-vis and solubility data. See DOI: 10.1039/b921081d

Table 1	Thermal	stability	of lactam-	-based	Brønsted-acidi	c ILs
---------	---------	-----------	------------	--------	----------------	-------

IL	[CP][BF ₄]	[CP][CH ₃ SO ₃]	[CP][NO ₃]	[CP][TFA]	[NMP][BF ₄]	[NMP][CH ₃ SO ₃]	[NMP][NO ₃]	[NMP][TFA]
$T_{d}{}^{a}$	168 °C	186 °C	100 °C	87 °C	130 °C	160 °C	78 °C	75 °C
" $T_{\rm d}$ was recorded with 10% of mass loss of IL.								

Experimental

General remarks

All commercial chemicals were used as received. NMR measurements were performed on a Brüker AV-400 Fourier transform NMR spectrometer using an inner capillary filled with CDCl₃ for ¹H and ¹³C NMR. Chemical shifts were reported in parts per million (ppm, δ). Thermal gravimetric analysis (TGA) was performed with a Simultaneous Thermal Analysis-STA 409EP. The thermal decomposition temperature (T_d) was recorded with 10% mass loss of lactam-based Brønsted-acidic ILs, with a scan rate of 10 °C min⁻¹ under a N₂ atmosphere. UV-visible spectroscopy was conducted on a Shimadzu 2100 UV-visible spectrophotometer.

Preparation and characterization

Two series of lactam-based Brønsted-acidic ILs [NMP][X] and [CP][X] (X = BF₄, NO₃, CH₃SO₃ and TFA (trifluoroacetate)) were synthesized according to the procedure previously reported in the literature.^{25,26} As an example, the Brønsted-acidic IL caprolactam trifluoroacetate ([CP][TFA]) was synthesized as following.

Benzene (30 mL) was added to a 100 mL flask containing 11.32 g of CP (0.10 mol) with stirring. Then, 11.40 g trifluoroacetic acid (0.10 mol) was added dropwise into the above flask, which was immersed in an ice bath, within *ca.* 20 min. After 4 h at room temperature, benzene was removed under reduced pressure. The resultant was further dried at 90 °C under 1-5 mmHg for 1 h, affording the IL [CP][TFA].

The NMR data for the IL [CP][TFA] were as follows: ¹H NMR (CDCl₃): 1.67–1.79 (m, 6H), 2.50 (q, J = 5.2, 2H), 3.28 (q, J = 5.6, 2H), 8.43 (s, 1H), 14.81 (s, 1H). ¹³C NMR (CDCl₃): 22.38, 28.07, 29.94, 34.83, 43.13, 110.83–119.39 (q, CF₃, J = 288.0), 160.80, 181.57. T_d ([CP][TFA]) = 87 °C.

Acidity measurement

The acidic scales of the lactam-based Brønsted-acidic ILs were measured by UV-vis spectra with basic indicators according to the procedure reported in the literature.^{25,27} Based on eqn (1), where H_0 is the Hammett acidity function which represents the relative acidity of IL; [I] and [IH⁺] are the molar concentrations of, respectively, the unprotonated and protonated forms of the indicator. Based on the Beer–Lambert law the absorption is proportional to the concentration of absorbing species in the material, and on condition of the same light path length, the ratio of [I]/[IH⁺] can be calculated by the absorbance difference of basic indicator measured after addition of lactam-based Brønsted-acidic ILs.

 $H_0 = pK(I) + \log([I]/[IH^+])$ (1)

Methyl yellow (MY) (15 mg L⁻¹, p K_a =3.3), 4phenylazodiphenylamine (PADA) (10 mg L⁻¹, p K_a =1.5) and 2-nitrophenylamine (NPA) (5 mg L⁻¹, p K_a =-0.2) in dichloromethane were chosen as the basic indicators. The concentration of each lactam-based Brønsted-acidic IL was set at 80 mmol L⁻¹ in dichloromethane.

Esterification procedure

The reaction was carried out in a glass reactor with a reflux condenser and oil-bath. The acid and alcohol were added to the lactam-based Brønsted-acidic IL. The esterification was performed under different profiles of reaction time and temperature with vigorous stirring. Qualitative and quantitative analyses were conducted with an Agilent 7890A/5975C GC/MS and a capillary GC (Rtx-1: $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$) equipped with a flame ionization detector, respectively. The concentration of reactant and product were calculated using butyl butyrate as an internal standard. After the reaction, the ester and IL were separated by decantation. The IL was reused after removal of water under 1–5 mmHg vacuum at 110 °C for 1 h.

Results and discussion

The lactam-based Brønsted-acidic ILs were synthesized with high yields of 92–98%. Most of them were miscible with polar organic solvents such as 1-butanol, acetonitrile, and acetic acid but insoluble or partly soluble in non-polar organic solvents such as benzene, ethyl ether, and *n*-butyl acetate. The solubility of ILs in reaction mixture can be measured according to the procedure described in the literature using UV-visible spectroscopy.²⁸ For instance, the solubility of IL [CP][CH₃SO₃] in *n*-butyl acetate was as low as 0.54 g per 100 mL, while the solubility was 194 g per 100 mL in acetic acid and 170 g per 100 mL in 1-butanol. The thermal stability of these Brønsted-acidic ILs was characterized by the thermal decomposition temperature (T_d) in Table 1 and was found to be in the range 75–186 °C.

The acidities of these Brønsted-acidic ILs, characterized as the value H_0 , are reported in Table 2. The results indicated that among the lactam-based Brønsted-acidic ILs studied, the IL [NMP][BF₄] had the strongest relative acidity of $H_0 = -0.25$, while the IL [CP][TFA] showed the weakest relative acidity of $H_0 = 4.56$. The relative acidities of the Brønsted-acidic ILs had the following order of H_0 value: [NMP][BF₄] (-0.25) > [CP][BF₄] (-0.22) > [NMP][CH₃SO₃] (0.95) > [CP][CH₃SO₃] (0.98) > [NMP][NO₃] (2.83) > [CP][NO₃] (2.94) > [NMP][TFA] (4.46) > [CP][TFA] (4.56). Clearly, the anions played a crucial role in defining the acidity of the Brønsted-acidic ILs. Changing the anions in the Brønsted-acidic ILs could bring about large differences in the H_0 value. For example, the H_0 values of ILs [CP][BF₄], [CP][NO₃] and [CP][TFA] were -0.22, 2.94 and 4.56, respectively. However, the effect of cations on the H_0 value was

 Table 2
 Calculation of Hammett function for different lactam-based

 Brønsted-acidic ILs
 Calculation of Hammett function for different lactam-based

Substance	$A_{ m max}$	[I]%	[HI]%	H_0 (±0.05)
NPA	2.46	100	0	
$[NMP][BF_4]^a$	1.16	47	53	-0.25
[CP][BF ₄] ^a	1.21	49	51	-0.22
PADA	2.44	100	0	
[NMP][CH ₃ SO ₃] ^b	0.57	89	11	0.98
[CP][CH ₃ SO ₃] ^b	0.53	96	4	0.95
MY	2.71	100	0	
[NMP][NO ₃] ^c	0.69	77.9	22.1	2.83
$[CP][NO_3]^c$	0.82	79.9	20.1	2.94
[NMP][TFA] ^c	2.52	94.8	5.2	4.46
[CP][TFA] ^c	2.57	93.0	7.0	4.56

^{*a*} NPA (2-nitrophenylamine) was used as basic indicator. ^{*b*} PADA (4-phenylazodiphenylamine) was used as basic indicator. ^{*c*} MY (methyl yellow) was used as basic indictor.

 Table 3
 Results of esterification of acetic acid with 1-butanol catalyzed

 by [CP][CH₃SO₃] under different conditions

Entry	Acid : butanol : IL (molar ratio)	Temp. (°C)	Time (h)	Acid conv. (%)	Ester selectivity (%)
1	5:5:1	30	0.5	67.4	100
2	5:5:1	30	2	91.6	100
3	5:5:1	30	4	94.8	100
4	5:5:1	30	6	97.2	100
5	5:6:1	30	4	98.5	100
6	5:5:2	30	4	95.1	100
7	8:8:1	30	4	91.1	100
8	5:5:1	100	4	100	95.0

Reaction conditions: 20 mmol acetic acid, 20 mmol 1-butanol and 4 mmol [CP][CH₃SO₃].

insignificant. For example, the H_0 values for ILs [CP][NO₃] and [NMP][NO₃] were 2.94 and 2.83, respectively.

Before investigating the acidity effect of lactam-based Brønsted-acidic ILs on their catalytic performances in the esterification, IL [CP][CH₃SO₃] was selected to optimize the reaction conditions, due to its immiscibility with ester and higher apparent viscosity. Conditions optimized included the molar ratio of reactants, reaction temperature and time profile. The results are listed in Table 3. It can be seen that 94.8% of acid conversion with 100% of ester selectivity could be obtained with 20% molar ratio of the catalyst to substrate at 30 °C for 4 h. Better results with 97.2% and 98.5% of ester yield could be obtained when the reaction time was prolonged to 6 h (Table 3, entry 4) or the concentration of 1-butanol was increased (Table 3, entry 5), respectively. It is also noteworthy that no significant increase either in acid conversion or ester selectivity occurred as a result of the increase of molar ratio of catalyst to substrate from 20% to 40% (Table 3, entries 3 and 6). A 100% conversion was obtained at the cost of the ester selectivity by increasing the reaction temperature to 100 °C (Table 3, entry 8). Therefore, in consideration of efficiency, we decided to carry out the reaction using a molar ratio of acid:alcohol:IL = 5:5:1 at $30 \degree C$ for 4 h.

Next, a set of lactam-based Brønsted-acidic ILs with different anions and cations were employed as catalysts for the esterification of acetic acid with 1-butanol. The results are summarized in Table 4. It can be seen that these catalysts showed moderate to high conversion and perfect selectivity at 30 °C. The by-products

 Table 4
 Results of esterification of acetic acid with 1-butanol catalyzed by different lactam-based Brønsted-acidic ILs

Entry	IL	Acid conv. (%)	Ester selectivity (%)
1	[CP][TFA]	69.4	100
2	[CP][NO ₃]	89.0	100
3	[CP][CH ₃ SO ₃]	94.8	100
4	[CP][BF₄]	92.8	100
5	[NMP][TFA]	74.1	100
6	[NMP][NO ₃]	89.5	100
7	[NMP][CH ₃ SO ₃]	95.5	100
8	[NMP][BF ₄]	93.0	100

Reaction conditions: 20 mmol acetic acid, 20 mmol 1-butanol and 4 mmol lactam-based Brønsted-acidic IL at 30 °C for 4 h.

such as ethers were not detected by capillary GC. Combined with the above-mentioned acidity order of these Brønstedacidic ILs ranked by H_0 , it was obvious that the acidity had a great effect on the catalytic performance of the esterification. The catalytic activities of these catalysts with the same anions but different cations were of an equal level. For example, in the presence of catalysts [CP][TFA] and [NMP][TFA], of which the acidity was in the weakest level among the catalysts investigated, the conversion of acetic acid was only 69.4% and 74.1%, respectively (Table 4, entries 1 and 5). The catalysts with stronger acidity, either with nitrate anion, such as [CP][NO₃] and [NMP][NO₃], or with tetrafluoroborate anion, such as [CP][BF₄] and [NMP][BF₄], showed higher activity for the esterification (Table 4, entries 2 and 6, 4 and 8). Compared with the catalysts having a nitrate anion, higher activity was obtained with use of [CP][BF₄] or [NMP][BF₄]. For instance, when the esterification was catalyzed by [CP][BF₄] or [NMP][BF₄], the conversion of acetic acid reached 92.8% and 93.0%, while about 89.0% and 89.5% was achieved in the cases of [CP][NO₃] or [NMP][NO₃], respectively. The above results revealed that the acidity of the lactam-based Brønsted-acidic ILs played a vital role in their catalytic performance for the esterification. The activities of the catalysts with the same anion but different cations were quite close to each other. This may be due to the feature of acid catalysis for the esterification.

The catalysts having a methyl sulfonate anion afforded the highest catalytic activity among those investigated. When the ILs [CP][CH₃SO₃] or [NMP][CH₃SO₃] were employed as catalysts for the esterification under identical conditions, the conversion of acetic acid reached 94.8% and 95.5%, respectively (Table 4, entries 3 and 7). However, since the esterification is a class of typical reversible reaction, the influence of ILs on the reaction rate is in large part attributable to an expected Le Chatelier effect in which a greater solubility of the IL catalyst in the reaction mixture slows down the reaction rate. For instance, the catalyst [CP][CH₃SO₃] was miscible with 1-butanol and acetic acid but almost immiscible with *n*-butyl acetate, so the ester formed could be separated from the layer of catalyst [CP][CH₃SO₃] and reaction mixture promptly, resulting in a faster esterification rate. However, the catalyst [CP][BF₄] was miscible with the ester and reaction mixture due to its good solubility in substrates and also in ester (142 g per 100 mL in n-butyl acetate), so it showed a slightly slower reaction rate than [CP][CH₃SO₃], although its acidity was stronger than [CP][CH₃SO₃] (Table 4, entries 3 and 4). Therefore, the acidity of lactam-based ILs having methyl

Table 5 Esterification of different carboxylic acids with alcohols catalyzed by IL [CP][CH₃SO₃]

Entry	Carboxylic acid	Alcohol	Temp. (°C)	Time (h)	Acid conv. (%)	Ester selectivity (%)	IL solubility in ester (g per 100 mL) ^a
1	Acetic acid	1,4-Butanediol	60	4	93.6	100 ^b	5.2
2	Lauryl acid	Methanol	30	8	92.1	100	1.3
3	Stearic acid	Methanol	60	8	91.8	100	2.9 ^c
4	Acetic acid	Benzyl alcohol	60	4	83.8	100	4.1
5 ^d	Oxalic acid	1-Butanol	60	4	93.1	100	8.0
6	Cyclopropanecarboxylic acid	Ethanol	30	8	87.0	100	8.6
7	Undecenoic acid	Methanol	30	8	89.4	100	3.9
8	Benzoic acid	Ethanol	60	8	84.0	100	8.0

Reaction conditions: 20 mmol carboxylic acid, 20 mmol alcohol and 4 mmol $[CP][CH_3SO_3]$. "The solubility of $[CP][CH_3SO_3]$ in corresponding ester was determined by UV-visible spectroscopy at 30 °C. "The total selectivity of mono- and diester." The solubility was measured at 60 °C. "Using 20 mmol of oxalic acid and 40 mmol of 1-butanol and the total selectivity of dibutyl oxalate and butyl oxalate.

Downloaded by Syracuse University on 13/05/2013 19:13:21. Published on 19 February 2010 on http://pubs.rsc.org | doi:10.1039/B921081D

sulfonate anions and their immiscibility with esters may have a synergistic effect on the catalytic performance for esterification.

To further verify the synergistic effect, the esterification of acetic acid and 1-butanol was carried out in ILs 1-butyl-3-methylimidazolium methanesulfonate ([BMIm][CH₃SO₃]) 1-(propyl-3-sulfonyl)-3-methylimidazolium trifluoand romethanesulfonate ([MIm(CH₂)₃SO₃H][TfO]). The catalyst [BMIm][CH₃SO₃] which shows non-acidity but good biphasic behaviour with n-butyl acetate (1.44 g per 100 mL) had negligible activity for the esterification, indicating that the acidity was the key for the activity of catalysts for the esterification. As for the catalyst [MIm(CH₂)₃SO₃H][TfO], it possessed stronger acidity $(H_0 = -1.8)$ and good biphasic behavior with the resultant esters (0.39 g per 100 mL). Accordingly, the higher conversion (98.5%) of acetic acid was obtained in a shorter reaction time of 1 h. Consequently, as a whole, as in inorganic acid catalysts, the stronger the acidity, the higher the catalytic activity of the lactam-based Brønsted-acidic ILs in the esterification. Furthermore, the synergistic effect of the acidity of ILs and their immiscibility with esters could enhance the catalytic activity of esterification.

The synergistic effect of the acidity of lactam-based ILs having a methanesulfonate anion and their immiscibility with esters was also valid in a variety of esterifications. Table 5 reports the esterification of different carboxylic acids with several alcohols catalyzed by the catalyst [CP][CH₃SO₃]. Since some typical carboxylic acids are solid at room temperature, the reaction temperature for these was set at 60 °C. Three typical aliphatic acids, namely acetic acid, lauryl acid and stearic acid, which have different chain lengths, were examined. Satisfactory results (Table 5, entries 1-4) were obtained, despite their different chain lengths, with prolonged reaction times. Oxalic acid, as a dibasic aliphatic acid, was esterified with two equivalents of 1-butanol at 60 °C for 4 h, and a conversion of 93.1% and selectivity of 100% to dibutyl oxalate was obtained (Table 5, entry 5). Alicyclic and unsaturated aliphatic acids, being different from the above saturated aliphatic acids, were also tested, with good results obtained. The conversions of cyclopropanecarboxylic acid and undecenoic acid reached 87.0% (Table 5, entry 6) and 89.4% (Table 5, entry 7) with 100% selectivity to the corresponding esters, respectively. For a typical aromatic acid, benzoic acid, a moderate result was obtained. When the reaction was carried out at 60 °C for 4 h, the conversion of benzoic acid was only 62.0%.

When the reaction time was prolonged to 8 h, the conversion increased to 84.0% (Table 5, entry 8). Therefore, the lactambased ILs having a methanesulfonate anion are versatile catalysts with high activity for the esterification of aliphatic or aromatic carboxylic acids.

The reusability of the catalyst $[CP][CH_3SO_3]$ is illustrated in Fig. 1. It can be seen that there was no obvious loss of catalytic activity for the esterification of acetic acid with 1-butanol after running consecutive recycling runs ten times. The conversion of acetic acid remained >93.0% and the selectivity to *n*-butyl acetate remained at 100%. The results indicate that lactam-based Brønsted-acidic ILs having a methanesulfonate anion are a class of robust and reusable catalysts for esterification under mild conditions.



Fig. 1 The recycling of $[CP][CH_3SO_3]$ IL for esterification. Reaction conditions: 60 mmol acetic acid, 60 mmol 1-butanol, and 12 mmol $[CP][CH_3SO_3]$ at 30 °C for 4 h.

Conclusions

In conclusion, several lactam-based Brønsted-acidic ILs were synthesized. These ILs were potentially efficient catalysts for esterification under mild reaction conditions without addition of any organic solvents or cocatalysts. The catalytic performance was dependent on the synergistic effect of the acidity of Brønsted-acidic ILs and their immiscibility with esters. The lactam-based Brønsted-acidic ILs having a methanesulfonate anion showed the best catalytic performance, with excellent reusability and stability.

Acknowledgements

The authors gratefully acknowledge the financial supports from the NSFC (20873108), the 973 program (2009CB939804) and the Key Scientific Project of Fujian Province (2009HZ0002-1).

Notes and references

- 1 P. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Chemistry*, Wiley, New York, 1999, ch. 5.
- 2 M. Hino and K. Arata, Appl. Catal., 1985, 18, 401.
- 3 A. Heidekum, M. A. Harmer and W. F. Hoelderich, *J. Catal.*, 1999, **181**, 217.
- 4 I. J. Dijs, H. L. F. van Ochten, C. A. van Walree, J. W. Geus and L. W. Jenneskens, J. Mol. Catal. A: Chem., 2002, 188, 209.
- 5 K. Inoue, M. Iwasaki and K. Matsui, U.S. Pat. 5241106 (1993).
- 6 R. A. Crane, S. H. Brown and L. De Caul, U.S. Pat. 5973193 (1999).
- 7 Y. D. Ma, Q. L. Wang, H. Yan, X. D. Ji and Q. Qiu, *Appl. Catal., A*, 1996, **139**, 51.
- 8 Y. Leng, J. Wang, D. R. Zhu, X. Q. Ren, H. Q. Ge and L. Shen, Angew. Chem., Int. Ed., 2009, 48, 168.
- 9 E. D. Bates, R. D. Mayton, I. Ntai and J. H. Davis, Jr, J. Am. Chem. Soc., 2002, 124, 926.
- 10 A. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr and R. D. Rogers, *Environ. Sci. Technol.*, 2002, 36, 2523.

- 11 C. D. Liang, J. F. Huang, Z. J. Li, H. M. Luo and S. Dai, *Eur. J. Org. Chem.*, 2006, 586.
- 12 H. Olivier-Bourbigou and L. Magna, J. Mol. Catal. A: Chem., 2002, 182–183, 419.
- 13 T. Welton, Chem. Rev., 1999, 99, 2071.
- 14 R. Sheldon, Chem. Commun., 2001, 2399.
- 15 Y. Deng, F. Shi, J. Peng and K. Qiao, J. Mol. Catal. A: Chem., 2001, 165, 33.
- 16 T. L. Greaves, A. Weerawardena, C. Fong, I. Krodkiewska and C. J. Drummond, J. Phys. Chem. B, 2006, 110, 22479.
- 17 T. L. Greaves and C. J. Drummond, Chem. Rev., 2008, 108, 206.
- 18 T. Joseph, S. Sahoo and S. B. Halligudi, J. Mol. Catal. A: Chem., 2005, 234, 107.
- 19 H. Zhu, F. Yang, J. Tang and M. He, Green Chem., 2003, 5, 38.
- 20 Z. F. Zhang, W. Z. Wu, B. X. Han, T. Jiang, B. Wang and Z. M. Liu, J. Phys. Chem. B, 2005, 109, 16176.
- 21 H. B. Xing, T. Wang, Z. H. Zhou and Y. Q. Dai, *Ind. Eng. Chem. Res.*, 2005, 44, 4147.
- 22 H. B. Zhang, F. Xu, X. H. Zhou, G. Y. Zhang and C. X. Wang, Green Chem., 2007, 9, 1208.
- 23 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weave, D. C. Forbes and J. H. Davis, J. Am. Chem. Soc., 2002, 124, 5962.
- 24 D. C. Forbes and K. J. Weaver, J. Mol. Catal. A: Chem., 2004, 214, 129.
- 25 Z. Y. Du, Z. P. Li, S. Guo, J. Zhang, L. Y. Zhu and Y. Q. Deng, *J. Phys. Chem. B*, 2005, **109**, 19542.
- 26 S. Guo, Z. Y. Du, S. G. Zhang, D. M. Li, Z. P. Li and Y. Q. Deng, *Green Chem.*, 2006, 8, 1.
- 27 C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts and B. Gilbert, J. Am. Chem. Soc., 2003, 125, 5264.
- 28 A. Beyaz, W. S. Oh and V. P. Reddy, Colloids Surf., B, 2004, 35, 119.