

SBA-15-functionalized TEMPO confined ionic liquid: an efficient catalyst system for transition-metal-free aerobic oxidation of alcohols with improved selectivity†

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A novel SBA-15-functionalized TEMPO confined ionic liquid [BMIm]Br was found to be a highly efficient and recyclable catalyst system for the transition-metal-free aerobic oxidation of a wide range of structurally diverse alcohols. Thanks to the strong physical confinement of the ionic liquid inside the mesochannels of SBA-15-supported TEMPO, the resulting solid catalyst showed improved selectivity in the aerobic oxidation of allylic alcohols. The catalyst can be recovered and re-used for at least 11 reaction runs without significant loss of either activity or confined IL.

Introduction

The selective oxidation of alcohols into carbonyl compounds is one of the most important reactions in both the industrial synthesis of fine chemicals and laboratory research.¹ This transformation has traditionally been performed with stoichiometric amounts of high-valence transition-metal salts or organic-based oxidants that generate relatively large amounts of metal-containing hazardous wastes and the reactions are usually run in chlorinated solvents.² However, the recent stringent environmental and legislative concerns demand greener methods with a high degree of chemoselectivity that minimize or eliminate the use of toxic and/or corrosive reagents and stop the formation of undesired by-products.³ As a consequence, the oxidation of alcohols with molecular oxygen in the presence of metal-catalysts has attracted a great deal of attention in recent years.^{4,5} Although interesting developments in improving catalytic activities and selectivities are evident, these methods are still using transition metal catalysts, which may possibly leave toxic traces of heavy metals in the products. Therefore, in order to avoid the use of transition metals, the development of new efficient and non-metallic catalysts for the aerobic oxidation of alcohols appears very appealing in view of so-called green and sustainable chemistry. Of particular interest in this field are catalytic systems involving the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in combination with a non-metallic co-catalyst, which have been increasingly explored for the oxidation of alcohols

using molecular oxygen as terminal oxidant.^{6,7} Along these lines, the first breakthrough metal-free aerobic oxidation of alcohols using a TEMPO/NaNO₂/Br₂ catalyst system was uncovered by Liang and Hu and co-workers.⁸ However, the use of chlorinated solvents and homogeneous, non-recyclable TEMPO make this route less attractive for practical purposes. To address some of these limitations, the same research group also developed various NaNO₂- and *t*-butylnitrite (TBN)-based systems in combination with TEMPO to catalyze the aerobic oxidation of alcohols.⁹ Meanwhile, He and co-workers have disclosed a metal-free catalytic system comprising TEMPO-functionalized imidazolium salt/NaNO₂/CO₂/H₂O for oxidation of alcohols in the presence of molecular oxygen.¹⁰ While this protocol demonstrates excellent performance in the oxidation of primary benzylic alcohols, the same transformations with either primary aliphatic or secondary alcohols gave moderate to low yields of the corresponding carbonyl compounds. On the other hand, quite recently, Studer and Wertz have described an innovative metal-free catalyst system consisting of homogeneous TEMPO and aqueous NH₂OH to accomplish the aerobic oxidation of a relatively wide range of alcohols, with good to excellent results.¹¹ However, despite these interesting achievements, this method requires a relatively high concentration of non-recyclable and expensive TEMPO (up to 4 mol%) and oxygen pressure up to 3 bar.

To address the recyclability of TEMPO while emphasizing the importance of metal-free aerobic oxidation of alcohols, we recently reported a durable and recyclable catalyst system comprising SBA-15 supported TEMPO/NaNO₂/*n*-Bu₄NBr for the aerobic oxidation of alcohols in acetic acid.¹² However, despite the high catalytic performance and recyclability of this system, our studies showed that the method is not suitable for acid-sensitive substrates and, more importantly, the oxidation of allylic alcohols to α,β -unsaturated carbonyl compounds could not be achieved using this protocol (*vide supra*).

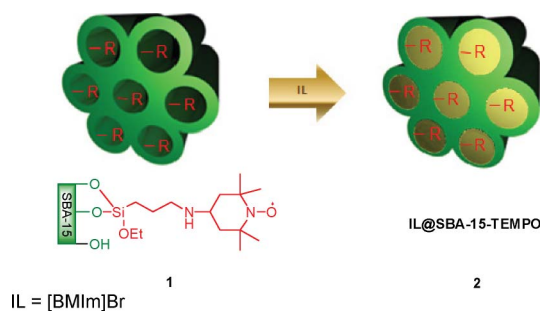
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† Electronic supplementary information (ESI) available: details of experimental procedure, N₂ adsorption-desorption isotherm for **1**, **2**, and the recovered **2**, BJH diagrams, and TEM image of the recovered **2**. See DOI: 10.1039/c1ob05178d

Herein we wish to report that filling mesochannels of SBA-15-functionalized TEMPO with 1-methyl-3-butylimidazolium (BMImBr) ionic liquid results in an efficient and recyclable catalyst system for the aerobic oxidation of various types of alcohols with improved selectivity under metal-free conditions.¹³ In particular, we found that the catalyst shows excellent selectivity and performance in the oxidation of allylic alcohols

Results and Discussion

The SBA-15 supported TEMPO **1** was initially prepared according to our previously reported protocol.^{12a} The obtained TEMPO-functionalized SBA-15 was then mixed with an acetone solution containing appropriate amounts of BMImBr and the mixture was stirred for 3 h at room temperature.^{14,15} To this end, the solvent was evaporated under reduced pressure to give a very fine bright yellow and free-flowing solid denoted as IL@SBA-15-TEMPO (Scheme 1, **2**).



Scheme 1 A schematic pathway for the preparation of SBA-15-functionalized TEMPO confined ionic liquid **2**.

The nitrogen adsorption–desorption experiments of **1** showed the BET (Brunauer–Emmett–Teller) surface area of 480 m² g^{−1}, the primary mesopore volume of 0.91 cm³ g^{−1}, and BJH (Barrett–Joyner–Halenda) average pore diameter of 6.18 nm.¹⁴ The materials typically showed a type IV N₂ sorption isotherm with a sharp hysteresis loop at relative pressure range $P/P_0 \sim 0.6$ – 0.8 , which is characteristic of ordered mesoporous solids with a narrow pore size distribution (Fig. 1).

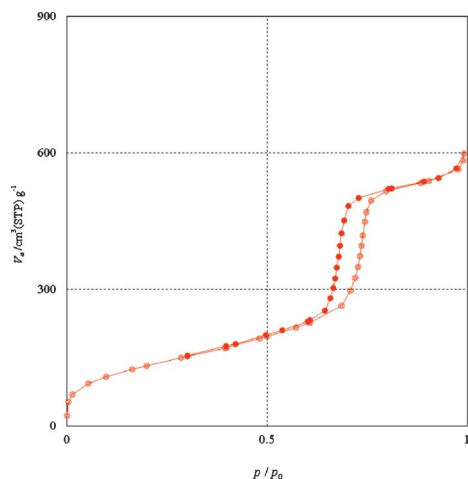


Fig. 1 The N₂ adsorption–desorption isotherm for SBA-15-functionalized TEMPO **1**.

On the other hand, the N₂ adsorption isotherm of **2**, as well as the BET surface area, was considerably different from **1**. The decrease in the BET surface area (29 m² g^{−1}) and mesopore volumes (0.1 cm³ g^{−1}) and the loss of the capillary condensation/evaporation N₂ isotherm clearly demonstrate that the loading of ionic liquid into the mesopores of **1** has successfully been achieved (Fig. 2).

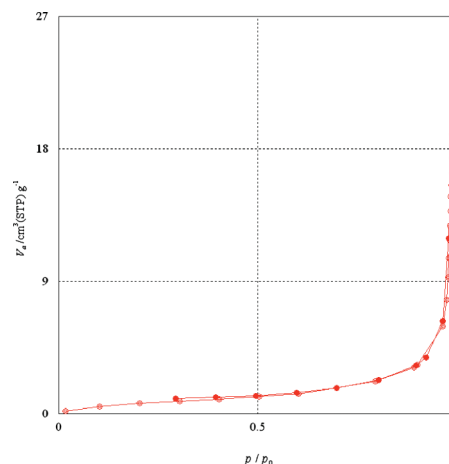


Fig. 2 The N₂ adsorption–desorption isotherm for SBA-15-functionalized TEMPO confined ionic liquid **2**.

The catalytic performance and selectivity of **2** was evaluated in the aerobic oxidation of benzyl alcohol as a model substrate, in the presence of molecular oxygen. The reactions were carried out in a batch reactor under an O₂ atmosphere at normal pressure, in the temperature range 30–80 °C. In this regard, the oxidation of benzyl alcohol took place smoothly in the presence of 1 mol% of **2**, 8 mol% of NaNO₂ and AcOH (0.3 mL) at 80 °C to give, after 3 h, the corresponding benzaldehyde in only 60% yield (Table 1, entry 1).

Interestingly, the use of TBN (8 mol%) instead of NaNO₂, gave quantitative yields of benzaldehyde (Table 1, entry 2). It should be also underlined that no significant oxidation took place in the absence of either TBN or **2** under the same reaction conditions

Table 1 Optimization of aerobic oxidation of benzyl alcohol catalyzed by **2**

$\text{C}_6\text{H}_5\text{CH}_2\text{OH} \xrightarrow[\text{AcOH, } T \text{ (}^\circ\text{C), NaNO}_2 \text{ or TBN, O}_2 \text{ (1 atm)}]{\text{IL@SBA-15-TEMPO (2)}} \text{C}_6\text{H}_5\text{CHO}$					
Run	$T/^\circ\text{C}$	2 (mol %)	NO source (mol %)	Time (h)	Yield (%) ^a
1	80	1	NaNO ₂ (8)	3.0	60
2	80	1	TBN (8)	2.0	>99
3	80	1	—	3.0	<1
4	80	—	TBN (8)	3.0	8
5	80	1	TBN (4)	2.5	>99
6	60	1	TBN (4)	2.8	>99
7	50	1	TBN (4)	2.8	>99
8	40	1	TBN (4)	3.3	>99
9	30	1	TBN (4)	5.0	59
10	40	0.5	TBN (4)	5.0	30
11	40	1	TBN (4)	3.0	<5 ^b

^a GC yields using internal standard method. ^b The catalyst **1** was used.

(Table 1, entries 3, 4). The impact of the reaction temperature and TBN loading were also surveyed, and we found that by decreasing the reaction temperature to 40 °C, the oxidation reaction still went to completion, with a slight increase in reaction times (Table 1, entries 5–8). It is also worth mentioning that decreasing the TBN loading from 8 mol% to 4 mol% did not significantly affect the total efficacy of the process (Table 1, entry 5). In a separate experiment, the use of **1** without the loaded ionic liquid as a catalyst was shown to afford much worse results, further confirming the beneficial role of the ionic liquid in obtaining acceptable conversions (Table 1, entry 11).

Having the optimized reaction conditions, we then investigated the generality of our catalyst system with respect to the alcohol structure (Table 2).

Along these lines, we found that various types of primary benzylic alcohols, including those bearing both electron-withdrawing and electron-donating groups, were selectively converted to the corresponding aromatic aldehydes in excellent yields under the optimal reaction conditions (Table 2, entries 1–13). Similarly,

2 showed excellent activity for the oxidation of substituted secondary benzylic alcohols using molecular oxygen to furnish the corresponding ketones in good to excellent yields (Table 2, entries 14–16). These results clearly demonstrate that electronic effects do not seem to have a significant effect on the reaction time and final product yields for electron-rich and electron-deficient benzylic substrates.


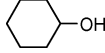
In general, the aerobic oxidation of alcohols that contain heteroatoms are considered highly challenging in most of the transition-metal catalyst systems, because their strong coordination to metal centers deactivates the catalyst. However, we found that our catalyst system is also highly effective for the oxidation of 4-(methylthio)benzyl alcohol, and 3-pyridinemethanol and affords the expected aldehydes in excellent yields and selectivities, further confirming the superior capability of **2** in oxidizing similar substrates (Table 2, entries 11, 12). Furthermore, allylic alcohols that are highly sensitive to acidic conditions could be effectively oxidized using the current method and gave excellent yields of the corresponding α,β -unsaturated carbonyl products, a feature not observed with most of the previous halogen-based TEMPO catalyzed protocols (Table 2, entries 17–19).^{9a-c,12a} It is very important to note that the same transformation using our previously reported SBA-15-TEMPO catalyst system **1** led to worse results for the aerobic oxidation of cinnamyl alcohol as a model substrate under the same reaction conditions (Table 2, entries 20, 21). These results clearly confirm that the confinement of ionic liquid molecules inside the mesochannels of SBA-15-functionalized TEMPO have a high impact in achieving improved selectivity in the oxidation of allylic substrates using the present protocol.¹⁶ Notably, this method was equally applicable to the oxidation of both primary and secondary aliphatic alcohols with slight modifications, giving the respective carbonyl compounds in moderate to excellent yield (Table 2, entries 22–26). Even cyclohexanol, which is considered a difficult substrate for TEMPO-mediated oxidation could be smoothly converted to cyclohexanone in a moderate yield of 67% under the described modified protocol (Table 2, entry 26). Remarkably, for all of the substrates studied, the method was also found to be highly selective for the oxidation of primary alcohols to the corresponding aldehyde without any detectable over oxidation to their carboxylic acids, even after prolonged reaction times.

The recyclability of **2** was also examined by isolating it from the reaction mixture of aerobic oxidation of benzyl alcohol through the successive microfiltration, washing with *n*-heptane and drying.¹⁷ The recycled catalyst was then successfully used in 11 successive reaction runs without any detectable loss of activity (Table 1S, ESI†).

Notably, N₂ adsorption–desorption analysis of the recovered catalyst **2** demonstrated that the leaching of ionic liquid [BMIm]Br was negligible in the recovered catalyst (Fig. 3). Moreover, elemental microanalysis data of the recovered catalyst clearly shows the loss of IL from recovered **2** under our described recovery procedure was less than 8% of the initial content in fresh IL@SBA-15-TEMPO, thus confirming the results obtained from N₂-sorption analysis.

Furthermore, no appreciable catalytic activity was observed from the residue of the *n*-heptane extraction of **2**, even after prolonged reaction times. Moreover, TEM images of the reused catalyst also indicate that the 2D-hexagonal (honeycomb) nanostructures of **2** largely survived and no detectable changes in

Table 2 Metal-free aerobic oxidation of alcohols catalyzed by SBA-15-functionalized TEMPO confined ionic liquid (**2**)^a

$\text{R}^1\text{CH(OH)R}^2 \xrightarrow[\text{AcOH, 40 }^\circ\text{C, TBN, O}_2]{\text{2 (1 mol\%)}} \text{R}^1\text{C(=O)R}^2$				
Run	R ¹	R ²	Time (h)	Yield (%) ^b
1	C ₆ H ₅	H	3.5	>99
2	4-Me-C ₆ H ₄	H	3	96
3	4-MeO-C ₆ H ₄	H	3.5	>99
4	3-NO ₂ -C ₆ H ₄	H	3.5	95
5	4-NO ₂ -C ₆ H ₄	H	3.5	98
6	3-Cl-C ₆ H ₄	H	3.5	99
7	3-Br-C ₆ H ₄	H	3.5	96
8	4-Br-C ₆ H ₄	H	3.5	>99
9	2,4-Cl ₂ -C ₆ H ₃	H	3.5	94
10	2-Naphthyl	H	3.5	>99
11	4-MeS-C ₆ H ₄	H	6	>99
12	3-Pyridyl	H	6	93
13	2-Furyl	H	3	98
14	C ₆ H ₅	Me	6	92
15	C ₆ H ₅	Et	6	91
16	C ₆ H ₅	C ₆ H ₅	9	89
17	Ph-CH=CH	H	15	99 ^c
18	Ph-CH=CH	C ₆ H ₅	17	99 ^c
19			17	>99 ^c
20	Ph-CH=CH-	H	15	— ^d
21	Ph-CH=CH-	H	15	18 ^e
22	Ph-CH ₂ CH ₂	H	3	94 ^f
23	CH ₃ (CH ₂) ₆	H	3	95 ^f
24	CH ₃ (CH ₂) ₃	H	3	87 ^f
25	CH ₃ (CH ₂) ₅	Me	5	>99 ^f
26			15	67 ^f

^a Conditions: **2** (1 mol%), TBN (4 mol%) at 40 °C unless otherwise stated.

^b GC yields using internal standard method. ^c Conditions: **2** (3 mol%), TBN (4 mol%) at 60 °C. ^d Conditions: **1** (3 mol%), NaNO₂ (10 mol%), *n*-Bu₄NBr (8 mol%) at 60 °C; mixture of unidentified products were formed.

^e Conditions: **1** (3 mol%), TBN (4 mol%) at 60 °C. ^f Conditions: **2** (2 mol%), TBN (15 mol%), NaBr (15 mol%), at 80 °C.

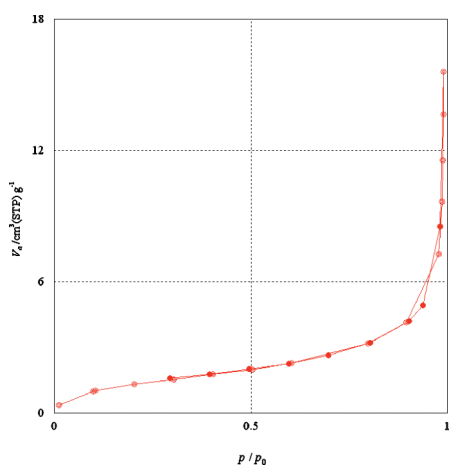


Fig. 3 The N_2 adsorption-desorption isotherm of the recovered SBA-15-functionalized TEMPO confined ionic liquid **2** from the aerobic oxidation of benzyl alcohol.

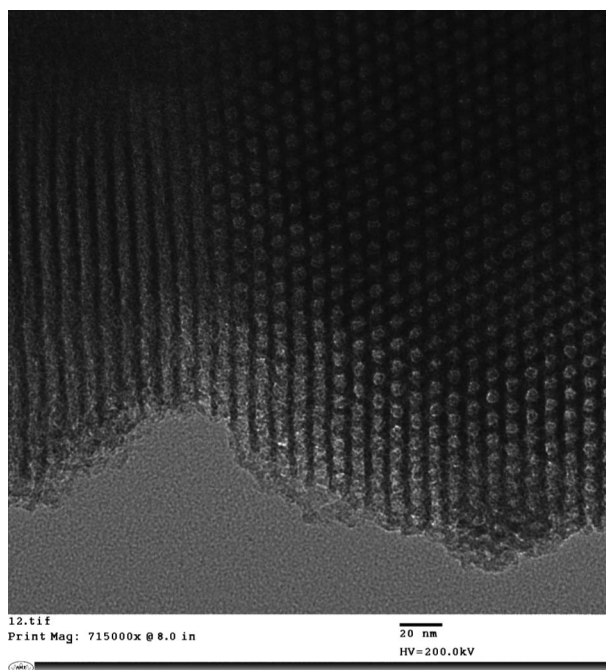


Fig. 4 A TEM image of recovered SBA-15-functionalized TEMPO confined ionic liquid **2** from the aerobic oxidation of benzyl alcohol.

the catalyst occurred during the catalysis and recycling stages (Fig. 4)

The exact role of the IL is not precisely clear to us at this stage. One explanation for the improved selectivity of **2** in comparison with the un-modified SBA-15-TEMPO in oxidizing allylic alcohols might be due to the highly polar environment provided by the IL inside the mesoporous channels, which likely speeds up the oxidation of TEMPO-OH by using *in situ* generated Br_2 to form the oxoammonium salt in the reaction catalytic cycle. This may in turn prevent (or slow down) the addition of bromine to double bonds in allylic systems. However, further in-depth investigation would be necessary to clarify the actual synergistic effect between the coated ionic liquid and immobilized TEMPO

moieties in achieving such selectivity. This study is currently ongoing in our laboratories.

Conclusions

In conclusion, we have demonstrated that the confinement of the ionic liquid [BMIm]Br inside the mesopores of SBA-15-functionalized TEMPO results in a highly recyclable catalyst system **2** for the selective and transition-metal-free aerobic oxidation of alcohols at normal oxygen pressures. In particular, this heterogeneous catalyst system remarkably showed much higher selectivities and efficiencies in the oxidation of allylic alcohols, in comparison with SBA-15-TEMPO not charged with IL. The catalyst can be recovered and reused for at least 11 reaction cycles without any significant loss of activity or selectivity. Notably, N_2 adsorption-desorption analysis of the recovered catalyst **2** demonstrated that the leaching of ionic liquid [BMIm]Br was negligible in the recovered catalyst. TEM images of the reused catalyst also demonstrated that in the nanostructures of **2**, no detectable changes in the catalyst nano-architecture occurred during the catalysis and recycling stages. Further studies to explore this strategy for other catalyst systems are ongoing in our laboratories.

Acknowledgements

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Notes and references

- (a) M. Hudlicky, *Oxidation in Organic Chemistry*, ACS Monograph Series, American Chemical Society, Washington DC, 1990; (b) R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1984.
- S. V. Ley and A. Madfin, *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and S. V. Ley, Pergamon, Oxford, U.K., 1991, vol. 7, pp 251–289.
- (a) J. H. Clark, *Green Chem.*, 1999, **1**, 1; (b) P. T. Anatas, and J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford, U.K., 1998.
- J.-E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, 2004.
- For more recent leading examples of transition-metal-catalyzed aerobic oxidations of alcohols, see (a) Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, *Angew. Chem., Int. Ed.*, 2007, **46**, 704; (b) S. S. Stahl, *Science*, 2005, **309**, 1824; (c) B. Karimi, S. Abedi, J. H. Clark and V. Budarin, *Angew. Chem., Int. Ed.*, 2006, **45**, 4776; (d) D. I. Enache, J. K. Edwards, P. London, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362; (e) A. Abad, P. Concepcion, A. Corma and H. Garcia, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066; (f) Z. Hou, N. Theyssen, A. Brinkmann and W. Leitner, *Angew. Chem., Int. Ed.*, 2005, **44**, 1346; (g) B. Karimi, A. Zamani and J. H. Clark, *Organometallics*, 2005, **24**, 4695; (h) N. Zheng and G. D. Stucky, *Chem. Commun.*, 2007, 3862; (i) K. Hara, S. Tayama, H. Kano, T. Masuda, S. Takakusagi, T. Kondo, K. Uosaki and M. Sawamura, *Chem. Commun.*, 2007, 4280; (j) L.-C. Wang, Y.-M. Liu, M. Chen, Y. Cao, H.-Y. He and K.-N. Fan, *J. Phys. Chem. C*, 2008, **112**, 6981; (k) F. Li, Q. Zhang and Y. Wang, *Appl. Catal., A*, 2008, **334**, 217; For an interesting recent study of aerobic oxidation of alcohols in supercritical carbon dioxide using supported palladium nanoparticles on hybrid mesoporous silica see: (l) Z. Hou, N. Theyssen, A. Brinkmann, K. V. Klementiev, W. Grünert, M. Bühl, W. Schmidt, B. Spliethoff, B. Tesche, C. Weidenthaler and W. Leitner, *J. Catal.*, 2008, **258**, 315; (m) Z. Hou, N. Theyssen and W. Leitner, *Green Chem.*, 2007, **9**, 127; (n) B. Karimi, A. Zamani, S. Abedi and J. H. Clark, *Green Chem.*, 2009, **11**, 109; (o) B. Karimi and F. Kabiri

- Esfahani, *Chem. Commun.*, 2009, 5555; (p) S. Kanaoka, N. Yagi, Y. Fukuyama, S. Aoshima, H. Tsunoyama, T. Tsukuda and H. Sakurai, *J. Am. Chem. Soc.*, 2007, **129**, 12060; (q) K. Kaizuka, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.*, 2010, **132**, 15096; (r) K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 10657; (s) P. Maity, C. S. Gopinath, S. Bhaduri and G. K. Lahiri, *Green Chem.*, 2009, **11**, 554; (t) Y. H. Ng, S. Ikeda, T. Harada, Y. Morita and M. Matsumura, *Chem. Commun.*, 2008, 3181; (u) B. Feng, Z. Hou, H. Yang, X. Wang, Y. Hu, H. Li, Y. Qiao, X. Zhao and Q. Huang, *Langmuir*, 2010, **26**, 2505; (v) F. Rajabi and B. Karimi, *J. Mol. Catal. A: Chem.*, 2005, **232**, 95.
- 6 For reviews of TEMPO-catalyzed alcohol oxidation, see: (a) A. E. J. de Nooy, A. C. Besemer and H. van Bakkum, *Synthesis*, 1996, 1153; (b) W. Adam, C. R. Saha-Moller and P. A. Ganeshpur, *Chem. Rev.*, 2001, **101**, 3499; (c) R. A. Sheldon, I. W. C. E. Arends, G.-J. ten Brink and A. Dijkman, *Acc. Chem. Res.*, 2002, **35**, 774; (d) R. A. Sheldon and I. W. C. E. Arends, *Adv. Synth. Catal.*, 2004, **346**, 1051; (e) N. Merbouth, J. M. Bobbitt and C. Brückner, *Org. Prep. Proced. Int.*, 2004, **36**, 1; (f) T. Volger and A. Studer, *Synthesis*, 2008, 1979; (g) J. M. Bobbitt, and C. Brückner, *Organic Reactions*, John-Wiley & Sons, New York, 2009.
- 7 For a recent review on aerobic oxidations in nitroxide-based oxidation protocols see: J. Piera and J.-E. Bäckvall, *Angew. Chem., Int. Ed.*, 2008, **47**, 3506. For a review on aerobic oxidation of alcohols using TEMPO in the presence of metal co-catalysts see: R. A. Sheldon and I. W. C. E. Arends, *J. Mol. Catal. A: Chem.*, 2006, **251**, 200.
- 8 R. Liu, X. Liang, C. Dong and X. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 4112.
- 9 (a) R. Liu, C. Dong, X. Liang and X. Hu, *J. Org. Chem.*, 2005, **70**, 729; (b) X. Wang, R. Liu, Y. Yin and X. Liang, *Chem.-Eur. J.*, 2008, **14**, 2679; (c) Y. Xie, W. M. Mo, D. Xu, Z. L. Shen, N. Sun, B. Hu and X. Hu, *J. Org. Chem.*, 2007, **72**, 4188; (d) X. He, Z. Shen, W. Mo, N. Sun, B. Hu and X. Hu, *Adv. Synth. Catal.*, 2009, **351**, 89.
- 10 (a) C.-X. Miao, L.-N. He, J. L. Wang and F. Wu, *J. Org. Chem.*, 2010, **75**, 257. For the use of recyclable acidic imidazolium salts in TEMPO-catalyzed aerobic oxidation of alcohols see: (b) C.-X. Miao, L.-N. He, J.-Q. Wang and J.-L. Wang, *Adv. Synth. Catal.*, 2009, **351**, 2209.
- 11 S. Wertz and A. Studer, *Adv. Synth. Catal.*, 2011, **353**, 69.
- 12 (a) B. Karimi, A. Biglari, J. H. Clark and V. Budarin, *Angew. Chem., Int. Ed.*, 2007, **46**, 7210. For more recent leading references on immobilized-TEMPO catalysts see: (b) J. Luo, C. Pardin, W. D. Lubell and X. X. Zhu, *Chem. Commun.*, 2007, 2136; (c) B. P. Mason, A. R. Bogdan, A. Goswami and D. T. McQuad, *Org. Lett.*, 2007, **9**, 3449; (d) A. Gheorghe, T. Chinnusamy, E. Cuevas-Yañez, P. Hilgers and O. Reiser, *Org. Lett.*, 2008, **10**, 4171; (e) A. P. Dobbs, M. J. Penny and P. Jones, *Tetrahedron Lett.*, 2008, **49**, 6955; (f) M. A. Subhani, M. Beigi and P. Eilbracht, *Adv. Synth. Catal.*, 2008, **350**, 2903; (g) A. Schätz, R. N. Grass, W. J. Stark and O. Reiser, *Chem.-Eur. J.*, 2008, **14**, 8262; (h) M. Kuroboshi, K. Goto and H. Tanaka, *Synthesis*, 2009, 903; (i) J.-P. B. Lindner, C. Röben, A. Studer, M. Stasiak, R. Ronge, A. Greiner and H.-J. Wendorff, *Angew. Chem., Int. Ed.*, 2009, **48**, 8874; (j) C. Röben, A. Studer, W. L. Hemme and H. Eckert, *Synlett*, 2010, 1110; (k) A. K. Tucker-Schwartz and R. L. Garrell, *Chem.-Eur. J.*, 2010, **16**, 12718. For recent interesting reviews on supported TEMPO catalysts see: (l) M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev.*, 2003, **103**, 3401; (m) F. Cozzi, *Adv. Synth. Catal.*, 2006, **348**, 1367.
- 13 For typical examples of coating ionic liquids onto silica-supported metal catalysts see: (a) Y. Gu, C. Ogawa, J. Kobayashi, C. Mori and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2006, **45**, 7217; (b) Y. Gu, C. Ogawa and S. Kobayashi, *Org. Lett.*, 2007, **9**, 175.
- 14 See Electronic Supplementary Information† for details.
- 15 The optimum amounts of ionic liquid needed to fill mesopores of SBA-15-TEMPO catalyst **1** was obtained based on the performance of IL@SBA-15-TEMPO **2** containing different amounts of [BMIm]Br in a typical aerobic oxidation of benzyl alcohol.
- 16 It has been shown that the coating of ionic liquid onto the silica supported sulfonic acid led to a catalyst system with improved selectivity in acid-catalyzed reactions: Y. Gu, A. Karam, F. Jérôme and J. Barrault, *Org. Lett.*, 2007, **9**, 3145.
- 17 In order to minimise the leaching of loaded ionic liquid during the recycling process it is crucial to use a non-polar solvent like *n*-heptane in washing stages.