Green Chemistry

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2014, **16**, 600

Received 10th July 2013,
Accepted 30th August 2013

DOI: 10.1039/c3gc41363b

www.rsc.org/greenchem

One-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol catalyzed by the Ru@ZIF-8 + CuO/basic ionic liquid system†

Honglei Fan, Yingying Yang, Jinliang Song, Guodong Ding, Congyi Wu, Guanying Yang and Buxing Han*

The development of green and efficient methods to transform lignin into fuels and high value-added chemicals is of great importance. In this work, we studied one-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol in a basic ionic liquid (BIL) 1-butyl-3-methylimidazolium 5-nitrobenzimidazolide, which acted as the solvent and provided the basic conditions required for the reactions. The effects of different factors such as the type of catalyst, reaction time, reaction temperature, and the amount of BIL on the oxidation reaction were investigated. It was demonstrated that the catalytic performance of individual Ru@ZIF-8 (zeolitic imidazolate framework-8) or CuO was very poor for the oxidation of veratryl alcohol to veratryl aldehyde. Interestingly, Ru@ZIF-8 + CuO was very efficient for the oxidation reaction and a high yield of veratryl aldehyde could be obtained, indicating the excellent synergistic effect of the two catalysts in the BIL. The veratryl aldehyde generated by the oxidation of veratryl alcohol could react directly with acetone to form 3,4-dimethoxybenzylideneacetone by aldol-condensation reaction catalyzed by the BIL in high yield.

Introduction

Transformation of biomass into high value-added chemicals and liquid fuels has received much attention in recent years. With its unique aromatic ring structures and low oxygen content, lignin is a promising component of biomass for the production of biofuels and aromatic chemicals.[1,2] Currently, the strategy used to produce biofuel from lignin is typically based on a two-step process,[3] depolymerization followed by upgrading. The depolymerization reactions can be principally divided into lignin cracking, hydrolysis reactions, catalytic reduction reactions, and catalytic oxidation reactions. In the oxidation reactions, lignin is converted to aldehydes selectively,[4] in which the number of carbon atoms can be further adjusted for the required fuels by aldol condensation reactions in the presence of a basic catalyst.

Model compounds are often used to study the reaction pathway and mechanism for lignin transformation. As a derivative of coniferyl alcohol (a primary monomer of lignin), veratryl alcohol bearing a 3,4-dimethoxy group has been extensively studied for understanding the chemistry of lignin valorization and exploring efficient transformation routes.[5] Veratryl alcohol can be oxidized into veratryl aldehyde by using different catalysts such as enzymes,[6] noble and non-noble metal porphyrin complexes,[7] cobalt(salen) complexes[8] and Co-zeolitic imidazolate frameworks (Co-ZIFs).[9] It is reported that the zeolitic imidazolate frameworks (ZIFs) like ZIF-8, -9, and -10 display excellent chemical and thermal stability, which have been developed for various applications such as gas storage[10] and alcohol oxidation.[11] Further, aldol condensation of aldehyde from lignin can be carried out to adjust the carbon atoms for obtaining fuels through the hydrodeoxygenation process.[12] The aldol condensation reaction can be performed using homogeneous catalysts like NaOH[13] or solid base catalysts[14] such as alkali metal and alkaline earth metal oxides.

Ionic liquids (ILs) with negligible vapor pressure, high thermal stability, and high gas solubility can be used as reaction media for replacing volatile and hazardous organic solvents.[15] Among them, basic ionic liquid (BIL) has been utilized in some base-catalyzed processes such as Heck,[16] Suzuki,[17] aldol condensation,[18] Henry[19] and Knoevenagel reactions.[20] The main advantage of using BILs is that they can function as both base and solvent. In addition, recent studies demonstrated the effectiveness of ILs for the dissolution of wood and lignocellulosic biomass.[21,22]

Herein, we conducted the one-pot reaction for veratryl alcohol oxidation followed by aldol-condensation in a BIL 1-butyl-3-methylimidazolium 5-nitrobenzimidazolide (the

---

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P.R. China. E-mail: hanbx@iccas.ac.cn; Fax: (+86) 10 6256 2821; Tel: (+86) 10 6255 9373

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc41363b

structure is shown in the ESI†), and Ru@ZIF-8 + CuO was used as a catalyst. It was demonstrated that veratryl alcohol could be oxidized into veratryl aldehyde very efficiently with high yield, and Ru@ZIF-8 and CuO exhibited an excellent synergistic effect to catalyze the oxidation reaction. Meanwhile, the BIL could also promote the following aldol-condensation reaction effectively. As far as we know, this is the first work on the catalytic oxidative reaction of lignin model compounds using Ru@ZIF-8 and CuO.

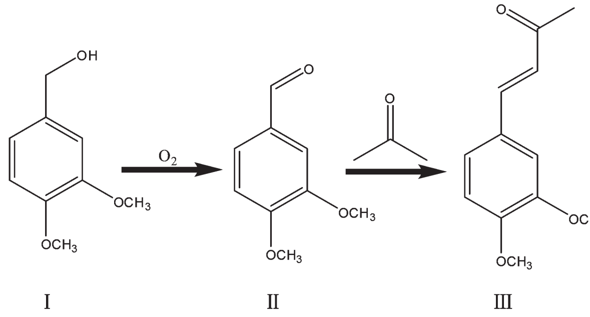
Experimental

Ethanol, sodium hydroxide, $Cu(NO_3)_2·3H_2O$, $Zn(NO_3)_2·6H_2O$, *N*,*N*-dimethyl formamide, acetone, diethyl ether, ethyl acetate, butyl alcohol, chloroform and methanol were obtained from the Beijing Chemical Reagents Company. Polyethylene glycol (MW = 200), 2-methyl imidazole, veratryl alcohol, veratryl aldehyde, 3,4-dimethoxybenzylideneacetone, $RuCl_3·3H_2O$ and 5-nitrobenzimidazole were provided by Alfa Aesar. 1-Butyl-3-methylimidazolium chloride was purchased from the Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Carbon dioxide and oxygen were provided by the Beijing Analytical Instrument Factory and their purity was >99.99%.

ZIF-8 was prepared according to methods reported in the literature.[23] Procedures to synthesize Ru/ZIF-8, copper oxide, and BIL as well as catalyst characterization are provided in the ESI.†

The X-ray diffraction (XRD) patterns were collected using a D/Max 2500 V/PC X-ray diffractometer with high intensity Cu Kα (40 kV, 200 mA) radiation. The high-resolution transmission electron microscopy (HRTEM) observation was carried out on a JEM 2011 at an accelerating voltage of 200 kV.

The reactions were conducted in an 8 mL reactor made of 316 stainless steel. In a typical experiment, the desired amounts of veratryl alcohol, catalyst, BIL, and water were loaded into the reactor. The reactor was placed in the preheated furnace of the desired temperature and air was removed under vacuum; then O_2 was charged into the reactor and the stirrer was started. After a suitable reaction time, the reactor was cooled in ice water. The products were extracted with ethyl acetate and analyzed by a gas chromatograph (GC) using an HP 4890 GC equipped with a flame ionization detector (FID), and butyl alcohol was used as the internal standard. To conduct the aldol-condensation reaction, acetone was added into the reactor after the oxidation reaction described above, and finally the amount of condensation product was determined quantitatively by GC. Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces. The yields are calculated as the mass of the products formed divided by the mass of the reactant initially loaded into the reactor.



Scheme 1 Sequential oxidation and aldol-condensation reactions of veratryl alcohol. **I**: veratryl alcohol; **II**: veratryl aldehyde; **III**: 3,4-dimethoxy-benzylideneacetone.

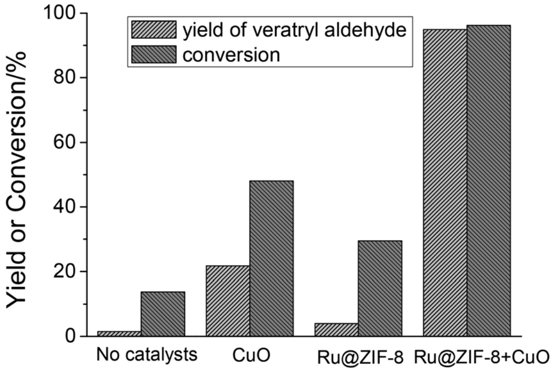


Fig. 1 Oxidation of veratryl alcohol with different catalysts. Reaction conditions: veratryl alcohol 0.1 g, BIL 1.0 g, O_2 0.5 MPa, distilled water 1.8 g, reaction temperature 130 °C, reaction time 55 min, and volume of the reactor 8 mL. If CuO is used, the amount is 0.02 g. If Ru@ZIF-8 (5 wt%) is used, the amount is 0.007 g.

Results and discussion

In our work, veratryl alcohol (**I**) was first oxidized into veratryl aldehyde (**II**), which was then reacted with acetone to produce 3,4-dimethoxybenzylideneacetone (**III**) by the well-known aldol-condensation reaction (Scheme 1).

Oxidation of veratryl alcohol

The performances of different catalysts were studied and the results are given in Fig. 1. As expected, the yield of veratryl aldehyde was very low without using the catalyst. When CuO or Ru@ZIF-8 was used individually, the yield of the product was also very low. Interestingly, when the two catalysts were used together (Ru@ZIF-8 + CuO), the yield could reach 94.9%, indicating an excellent synergistic effect of the two catalysts.

It was reported that in the presence of Ru nanocatalysts, the alcohol first combined with Ru to form Ru-alcoholate species and then β-hydride was eliminated to produce the corresponding aldehyde and a Ru hydride species. Subsequently, the Ru hydride species reacted with O_2 to produce water and complete the cycle.[24] For the CuO catalyst, alcohols were converted

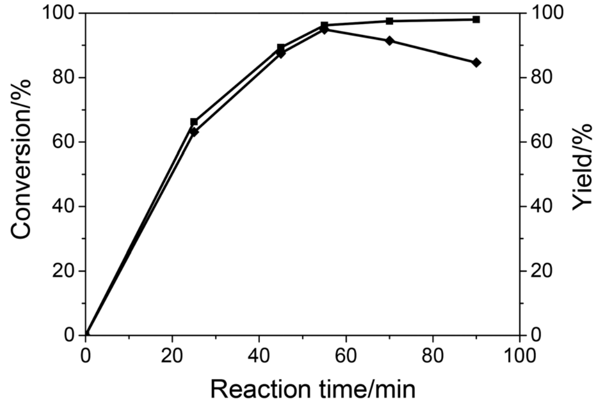


Fig. 2 Effect of reaction time on the oxidation of veratryl alcohol. Reaction conditions: veratryl alcohol 0.1 g, BIL 1.0 g, CuO 0.02 g, Ru@ZIF-8 (5 wt%) 0.007 g, O_2 0.5 MPa, distilled water 1.8 g, reaction temperature 130 °C, and volume of the reactor 8 mL.

into aldehydes or ketones by the dehydrogenation process.[25] The mechanism of the synergistic effect between Ru@ZIF-8 and CuO is very interesting and needs to be studied further.

The XRD patterns of the CuO particles are consistent with that in the JCPDS database, and the XRD patterns of the ZIF-8 are the same as that reported in the literature[23] (Fig. S1†). The TEM images of the Ru@ZIF-8 and CuO particles are shown in Fig. S2.† The diameter of Ru particles in the catalyst Ru@ZIF-8 was in the range of 3 to 5 nm, and the size of CuO particles was in the micron scale.

In the following, the effects of reaction parameters were further studied using combined catalysts. The dependence of the transformation of veratryl alcohol on reaction time is shown in Fig. 2. The conversion increased with reaction time and reached a plateau after 70 minutes. The yield increased with reaction time and reached a maximum at 55 minutes. The yield of veratryl aldehyde could reach 94.9%. As we know, oxidation of an alcohol is a cascade reaction, *i.e.*, the produced aldehyde can be further oxidized. In the meantime, for the aldehydes without active hydrogen at the α site, disproportionation reaction can occur to produce equimolar alcohol and acid under the basic conditions. Therefore, oxidation of veratryl alcohol and disproportionation of veratryl aldehyde occurred in the reaction system. After optimum reaction time, more aldehyde was converted by disproportionation reaction and overoxidation reaction. So, the yield of veratryl aldehyde decreased with reaction time after the maximum.

Ru@ZIF-8 catalysts containing different amounts of Ru were used to catalyze the reaction. The results are shown in Fig. 3. The conversion increased as the loading amount of Ru was changed from 2.5 to 5.5%. The yield of veratryl aldehyde increased first and decreased after the loading amount of Ru exceeded 5%. Generally, increasing the amount of active components is favorable for the conversion of reactants. But for cascade reactions like the oxidation of alcohol, catalytic sites also promote further transformation of the produced products. For the reaction studied in this work, transformation of the produced compounds became dominant after the loading amount of Ru exceeded 5 wt%, leading to a decrease in yield.

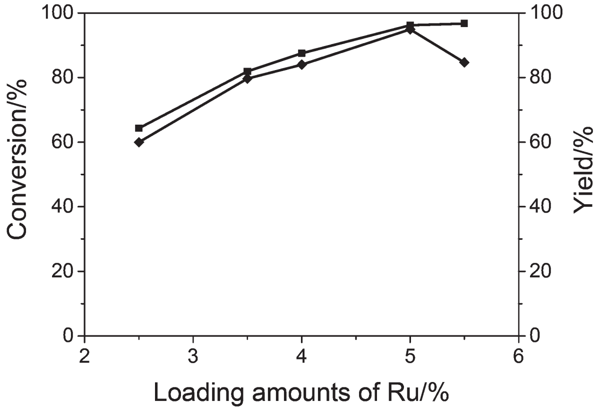


Fig. 3 Effect of loading amount of Ru in the Ru@ZIF-8 on the oxidation of veratryl alcohol. Reaction conditions: veratryl alcohol 0.1 g, BIL 1.0 g, CuO 0.02 g, Ru@ZIF-8 0.007 g, O_2 0.5 MPa, distilled water 1.8 g, reaction temperature 130 °C, reaction time 55 min, and volume of the reactor 8 mL.

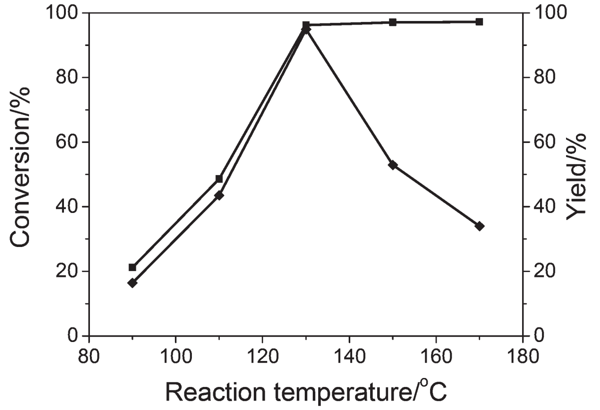


Fig. 4 Effect of reaction temperature on the oxidation of veratryl alcohol. Reaction conditions: veratryl alcohol 0.1 g, BIL 1.0 g, CuO 0.02 g, Ru@ZIF-8 (5 wt%) 0.007 g, O_2 0.5 MPa, distilled water 1.8 g, reaction time 55 min, and volume of the reactor 8 mL.

The effects of reaction temperature on the formation of veratryl aldehyde were studied in the range of 90 to 170 °C, and the results are shown in Fig. 4. The conversion of veratryl alcohol increased in the range of 90 to 130 °C, and remained unchanged with further increasing the temperature. In the temperature range of 90 to 130 °C, the effect of temperature on yield is significant, and the maximum yield was obtained at 130 °C. The temperature affected the yield in two opposite ways. On the one hand, the conversion of the reactant increased with increasing temperature, which was favorable for enhancing the yield of the product. On the other hand, elevating the temperature also promoted the occurrence of side reactions. The competition of the two factors resulted in the maximum of the yield.

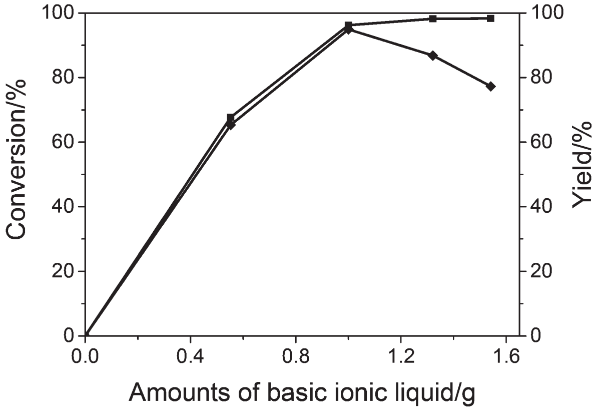


Fig. 5 Effect of added amount of BIL on the oxidation of veratryl alcohol. Reaction conditions: veratryl alcohol 0.1 g, CuO 0.02 g, Ru@ZIF-8 (5 wt%) 0.007 g, O_2 0.5 MPa, distilled water 1.8 g, reaction temperature 130 °C, reaction time 55 min, and volume of the reactor 8 mL.

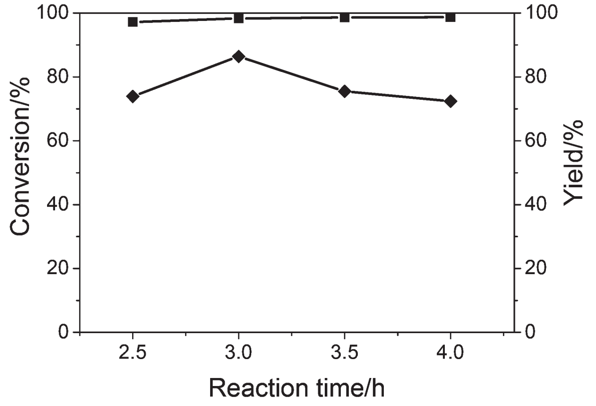


Fig. 6 Effect of reaction time of the aldol-condensation on the yield of 3,4-dimethoxybenzylideneacetone for the one-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol (Scheme 1). Reaction conditions for the oxidation of veratryl alcohol to form veratryl aldehyde were the same as those given in Fig. 1 using Ru@ZIF-8 + CuO as the catalyst. Reaction conditions for aldol-condensation: acetone 0.35 g, reaction temperature 85 °C, and volume of the reactor 8 mL.

Fig. 5 shows the dependence of the conversion of the reactant and the yield of the product on the amount of BIL used in the reaction. When the amount of BIL increased from 0.55 to 1.54 g, the conversion increased at first and then reached a plateau. The maximum yield could be observed when the amount of BIL was 1.0 g. The BIL in our work contains the imidazole anion, which can combine with protons in water, and hydroxide anions are formed. It is known that the hydroxide anion is helpful for the deprotonation of veratryl alcohol, thereby promoting the formation of veratryl aldehyde.[26] So, yield increased with the addition of the IL continuously at the beginning. At the same time, the degree of overoxidation and disproportionation reactions became larger with increasing the amount of BIL, leading to a decrease of the yield of veratryl aldehyde.

We carried out the experiment using 1.0 g of BIL without water. It was found that the yield of veratryl aldehyde was only 2.8%. This showed that water in the reaction system was necessary to guarantee that there is sufficient amount of hydroxide anions in the reaction system.

Sequential oxidation and aldol-condensation reactions of veratryl alcohol

We also studied the one-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol to produce **III** (Scheme 1). The oxidation of veratryl alcohol to form veratryl aldehyde was first conducted using Ru@ZIF-8 + CuO as the catalyst under the conditions given in Fig. 1. After oxidation to form veratryl aldehyde, the oxygen in the reactor was removed. Then acetone was added into the reactor, allowing the aldol-condensation reaction to occur. Fig. 6 shows the conversion of veratryl alcohol and the yield of product **III** as a function of reaction time. There was also a maximum in the yield *vs.* reaction time curve. It is known that the aldol-condensation reaction involves three steps: enolization, addition, and dehydration.[27] For base catalyzed aldol condensation, deprotonation of acetone is the rate determining step and an enolate anion is formed. With a long reaction time, the target product 3,4-dimethoxybenzylideneacetone could react with another molecular veratryl aldehyde to produce the further condensation product. Thus, the yield of product **III** decreased due to the occurrence of a side reaction.

Conclusions

We have studied the one-pot sequential oxidation and aldol-condensation reactions of veratryl alcohol in a BIL, which functions as both base and solvent for the reactions. It is found that Ru@ZIF-8 or CuO cannot catalyze the oxidation of veratryl alcohol to veratryl aldehyde effectively. However, Ru@ZIF-8 and CuO show an excellent synergistic effect to catalyze the oxidation reaction, and the reaction can proceed very efficiently in the BIL using a small amount of Ru@ZIF-8 + CuO catalyst. There is a maximum in the yield *vs.* reaction time curve, the yield *vs.* reaction temperature curve, and the yield *vs.* the amount of IL curve because the product veratryl aldehyde can be further converted. Under the optimized reaction conditions, the yield of veratryl aldehyde can be as high as 94.9%. Meanwhile, the BIL can promote an aldol-condensation reaction between veratryl aldehyde and acetone to produce 3,4-dimethoxybenzylideneacetone. The Ru@ZIF-8 + CuO/BIL is an excellent catalytic system for the one-pot sequential oxidation, and the yield of 3,4-dimethoxybenzylideneacetone can reach 86.4%. We believe that the combination of BILs and suitable catalysts opens the way for developing greener and more efficient methods to transform lignin-related compounds as well as the catalytic valorization of lignin.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (21173234, 21003133, and 21133009) and the Chinese Academy of Sciences (KJCX2.YW.H30) for financial support.

Notes and references

1 J. M. Cho, S. Chu, P. J. Dauenhauer and G. W. Huber, *Green Chem.*, 2012, **14**, 428–439.

2 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.

3 N. Yan, Y. Yuan, R. Dykeman, Y. Kou and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5549–5553.

4 A. Rahimi, A. Azarpira, H. Kim, J. Ralph and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 6415–6418.

5 J. Zakzeski, P. C. A. Bruijnincx and B. M. Weckhuysen, *Green Chem.*, 2011, **13**, 671–680.

6 M. Diaz-Gonzalez, T. Vidal and T. Tzanov, *Appl. Microbiol. Biotechnol.*, 2011, **89**, 1693–1700.

7 F. Cui and D. Dolphin, *Can. J. Chem.*, 1992, **70**, 2314–2318.

8 K. Kervinen, H. Korpi, M. Leskelä and T. Repo, *J. Mol. Catal. A: Chem.*, 2003, **203**, 9–19.

9 J. Zakzeski, A. D. ebczak, P. C. A. Bruijnincx and B. M. Weckhuysen, *Appl. Catal., A*, 2011, **394**, 79–85.

10 A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58–67.

11 A. Corma, H. Garcia, F. X. Llabrés and I. Xamena, *Chem. Rev.*, 2010, **110**, 4606–4655.

12 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.

13 C. J. Barrett, J. N. Chheda, G. W. Huber and J. A. Dumesic, *Appl. Catal., B*, 2006, **66**, 111–118.

14 I. Sádabaa, M. Ojedaa, R. Mariscala, R. Richardsb and M. López Granados, *Catal. Today*, 2011, **167**, 77–83.

15 H. Hosseini-Monfared, H. Meyer and C. Janiak, *J. Mol. Catal. A: Chem.*, 2013, **372**, 72–78.

16 S. A. Forsyth, U. Frohlich, P. Goodrich, H. Q. N. Gunaratne, C. Hardacre, A. McKeown and K. R. Seddon, *New J. Chem.*, 2010, **34**, 723–731.

17 M. Gruttadauria, L. A. Bivona, P. Lo Meo, S. Riela and R. Noto, *Eur. J. Org. Chem.*, 2012, 2635–3642.

18 S. Abello, F. Medina, X. Rodriguez, Y. Cesteros, P. Salagre, J. E. Sueiras, D. Tichit and B. Coq, *Chem. Commun.*, 2004, 1096–1097.

19 T. Jiang, H. X. Gao, B. X. Han, G. Y. Zhao, Y. H. Chang, W. Z. Wu, L. Gao and G. Y. Yang, *Tetrahedron Lett.*, 2004, **45**, 2699–2701.

20 C. Paun, J. Barklie, P. Goodrich, H. Q. N. Gunaratne, A. McKeown, V. I. Parvulescu and C. Hardacre, *J. Mol. Catal. A: Chem.*, 2007, **269**, 64–71.

21 A. Brandt, J. Grasvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550–583.

22 A. Casas, S. Omar, J. Palomar, M. Oliet, M. V. Alonso and F. Rodriguez, *RSC Adv.*, 2013, **3**, 3453–3460.

23 L. T. L. Nguyen, K. K. A. Le and N. T. S. Phan, *Chin. J. Catal.*, 2012, **33**, 688–696.

24 M. Lakshmi Kantam, U. Pal, B. Sreedhar, S. Bhargava, Y. Iwasawa, M. Tada and B. M. Choudary, *Adv. Synth. Catal.*, 2008, **350**, 1225–1229.

25 I. Park, J. Lee, Y. Rhee, Y. Hanb and H. Kim, *Appl. Catal., A*, 2003, **253**, 249–255.

26 K. Kervinen, H. Korpi, M. Leskelä and T. Repo, *J. Mol. Catal. A: Chem.*, 2003, **203**, 9–19.

27 R. W. Snell, E. Combs and B. H. Shanks, *Top. Catal.*, 2010, **53**, 1248–1253.