ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

An efficient ligand free chemoselective transfer hydrogenation of the olefinic bonds by palladium nanoparticles in aqueous reaction medium

Dattatraya B. Bagal*[a]* and Bhalchandra M. Bhanage,*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

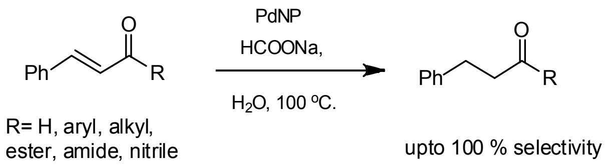
A highly efficient ligand free catalytic system was developed for chemoselective transfer hydrogenation of α,β-unsaturated carbonyl compounds by palladium nanoparticles (PdNPs) in aqueous reaction medium. The developed methodology offers chemoselective 1,4-reduction of various α,β-unsaturated carbonyl compounds such as carbonyls, amides, esters and nitrile with excellent chemoselectivity and effective catalyst recyclability.

Continuously growing interest in the hydrogenation reaction is dictated by a wide range of application in fine chemicals, agrochemicals and various valuable materials.[1-3] A selective hydrogenation of the olefinic bond of α,β-unsaturated carbonyl compounds to the saturated carbonyl compounds is challenging task since saturated carbonyl compounds are widely used as intermediates for the synthesis of various biologically active compounds.[4] In contrast, the selective reduction of the carbonyl group of α,β-unsaturated carbonyls to allylic alcohols have been achieved with relative ease.[5] In particular, conventional hydrogenation reaction uses hazardous molecular hydrogen and requires sophisticated instrument (autoclave), whereas transfer hydrogenation[6] process circumvents use of hydrogen gas and autoclave hence is easy to execute.

Not surprisingly, hydrogenation is one of the most broadly studied area of the organometallic chemistry. Various transition metal complexes such as palladium,[7] iridium,[8] rhodium,[9] ruthenium,[10] and other metal complexes[11] were used for chemoselective hydrogenation of olefinic double bond of α,β-unsaturated carbonyl compounds. More recently use of palladium/magnesium-lanthanum mixed oxide catalysts were reported by Kantam and co-workers for chemoselective reduction of olefinic bond using molecular hydrogen.[12] Burri and co-workers explored palladium nanoparticles immobilized on APTES functionalized SBA-15 for hydrogenation reaction using molecular hydrogen.[13] Moreover, Zhang et al. used pincer Pd complexes for transfer hydrogenation of α,β-unsaturated carbonyls with alcohol as a hydrogen source. [14]

However, the reported methods have disadvantages such as use of expensive metal and ligands, use of molecular hydrogen, low chemoselectivity, and use of hazardous organic solvents. Furthermore, the majority of earlier reported protocols are homogeneous which creates difficulty in recycling the precious metal catalyst thus limits their applications. In view of this, development of improved methodology with greener and economical catalytic system which facilitates the reuse of expensive metal catalyst which can be efficiently catalyse chemoselective transfer hydrogenation of α,β-unsaturated carbonyls is still challenging.

Nowadays, synthesis of metal nanoparticles (NPs) have received great attention due to their potential application in catalysis.[15] The high volume to mass ratio reveal high surface area results into high catalytic activity and hence required less catalyst concentration compared to bulk. In addition to this, nanocatalysts could be reused for further reactions. Also nanoparticles show high selectivity at high conversion rate under mild reaction conditions.[16] In continuation to the application of nanocatalyst in various organic transformations, the use of palladium nanoparticles (PdNPs) in catalysis has fascinated much interest.[17] In this regard, an efforts were taken to utilize PdNPs for chemoselective transfer hydrogenation reaction.



Scheme 1 Chemoselective transfer hydrogenation of α,β-unsaturated carbonyl compounds

Continuing the exploration of the facile protocol for the hydrogenation reactions with transition metal catalysts and being interested in transfer hydrogenation reactions,[18] we have tested the feasibility of PdNPs for the reduction of the α,β-unsaturated carbonyl compounds. Herein, we report highly chemoselective ligand free protocol for transfer hydrogenation of α,β-unsaturated carbonyl compounds catalysed by PdNPs in aqueous reaction media.

Results and discussion

The synthesis of palladium nanoparticles (PdNPs) were carried

---

[a] *Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai- 400 019, India. Fax: +91- 22 2414 5614; Tel: + 91- 22 3361 1111/2222; E-mail: bm.bhanage@gmail.com; bm.bhanage@ictmumbai.edu.in (B. M. Bhanage).*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

out using $PdCl_2$ as a precursor, citric acid as a greener reducing agent and polyvinyl pyrrolidone (PVP) as a capping agent by concentrated solar energy in the aqueous reaction medium (see the ESI†).[19] The characterization of prepared Pd (0) nanoparticles was carried out by using various analytical techniques such as field emission gun-scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM), and electron dispersive X-ray spectral (EDAX) analysis (Fig. 1-3). The size and morphology of synthesized PdNPs were determined by FEG-SEM and TEM analysis (Fig. 1 and 2). The Transmission Electron Microscopy (TEM) image confirmed that the obtained particles are in the nano region with uniform size ranging from 25 nm to 40 nm. The EDS spectrum shows that the prepared PdNPs contains palladium metal only (Fig. 3).

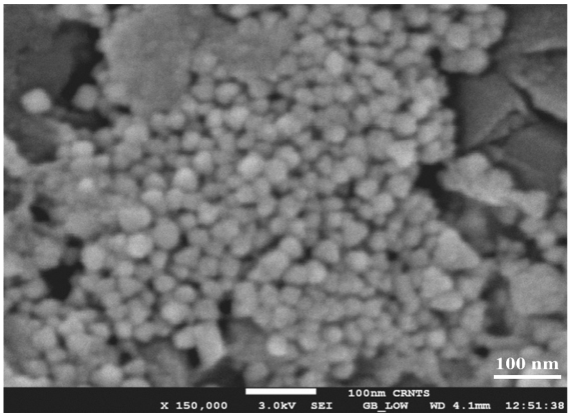


Figure 1 FEG-SEM image of synthesized palladium nanoparticles.

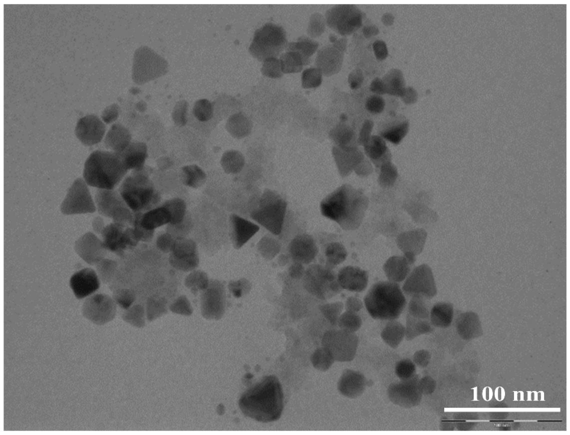


Figure 2 TEM image of synthesized palladium nanoparticles.

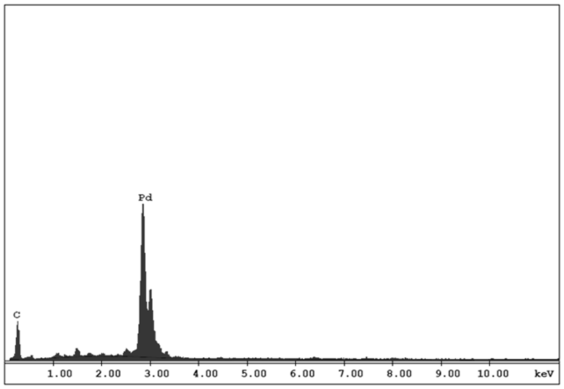


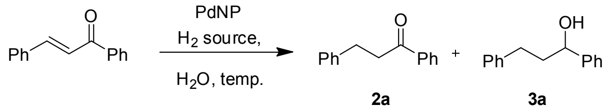
Figure 3 EDS pattern of synthesized Palladium nanoparticles

The prepared palladium nanoparticles solution was then diluted up to 100 mL with deionised water to make concentration of 1 mol % and used as a stock solution for the transfer hydrogenation of α,β-unsaturated carbonyls.

In order to optimize the reaction conditions, initial studies were conducted using PdNPs as a choice of catalyst and HCOONa as a hydrogen source at reflux reaction temperature for chemoselective transfer hydrogenation of the benzylideneacetophenone as a model reaction. A series of experiments were performed to optimize various reaction parameters such as effect of hydrogen donor, reaction temperature, time and the results obtained are summarized in Table 1.

Initially, we screened the effect of various hydrogen donors on transfer hydrogenation reaction (Table 1, entries 1-4), it was observed that 3 mmol of HCOONa gave 99 % conversion with excellent chemoselectivity of the desired product (Table 1, entry 1), while HCOOK and $HCOONH_4$ (Table 1, entries 2-3) gave slightly lower conversion, a mixture of HCOOH+Et_3N (1:1) (Table 1, entry 4) as a hydrogen source provided 95 % conversion of the starting material. We found that using 1.5 mmol of HCOONa provided 63 % conversion with 97 % selectivity of the desired product (Table 2, entry 5), while further increase in the amount of HCOONa, the selectivity decreases slightly with further reduction of carbonyl group (Table 1, entry 6).

Table 1 Effect of reaction parameters on transfer hydrogenation of benzylideneacetophenone[a]

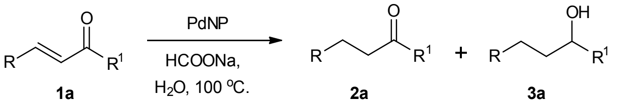


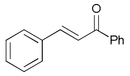
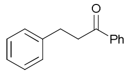
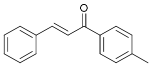
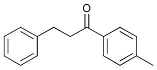
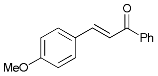
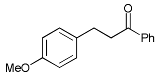
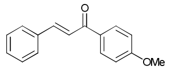
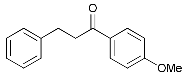
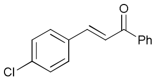
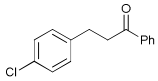
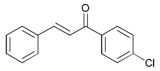
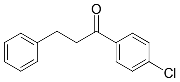
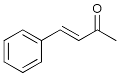
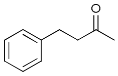
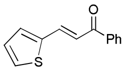
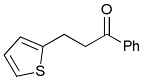
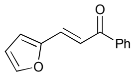
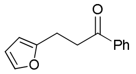
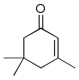
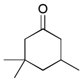
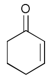
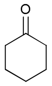
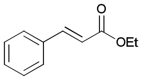
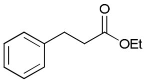
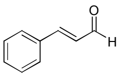
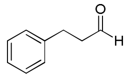
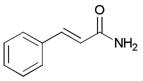
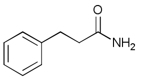
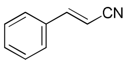
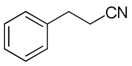
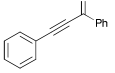
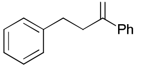
Entry	H_2 source	H_2 source (mmol)	Temp (°C)	Time (h)	Conv.[b] (%)	Selectivity[c] (**2a**:**3a**)
Effect of hydrogen donors						
1	HCOONa	3	100	8	99	99:1
2	HCOOK	3	100	8	78	98:2
3	$HCOONH_4$	3	100	8	67	97:3
4	HCOOH+ Et_3N	3	100	8	95	98:2
5	HCOONa	1.5	100	8	63	97:3
6	HCOONa	5	100	8	99	93:7
Effect of temperature						
7	HCOONa	3	25	8	36	99:1
8	HCOONa	3	50	8	57	99:1
9	HCOONa	3	70	8	78	99:1
Effect of time						
10	HCOONa	3	100	4	53	99:1
11	HCOONa	3	100	6	87	99:1

[a]Reaction conditions: benzylideneacetophenone (1 mmol), PdNPs (1 mol % stock solution in 5 mL deionised water), temperature (100 °C). [b]Conversion based on GC analysis. [c]Selectivity based on GCMS analysis.

Nextly, we examined the effect of temperature on reaction outcome; reactions were carried out at different temperatures ranging from room temperature to reflux (Table 1, entries 1, 7-9). It was observed that at 25 °C the yield of the desired product was low (36%) whereas, with increasing reaction temperature gradually from room temperature to reflux temperature, 99% conversion with 99% selectivity of the desired product was

Table 2 Chemoselective transfer hydrogenation of α,β-unsaturated carbonyl compounds[a]



Entry	Substrate	Product	Conversion[b] (%)	Selectivity[c] (2a:3a)
1			99	99:1
2			99	98:2
3			99	98:2
4			99	97:3
5			91	92:08
6			87	89:11
7			97	98:2
8			94	97:3
9			95	98:2
10			98	97:2
11			99	97:2
12			84	100:0
13			89	93:7
14			79	100:0
15			98	100:0
16[d]			99	98:2

aReaction conditions: substrate (1.0 mmol), PdNPs (1 mol % in 5 mL deionised water), HCOONa (3 mmol), temperature (100 °C), time (8 h). [b]Conversion based on GC analysis. [c]Selectivity based on GCMS analysis. [d]Required 6 mmol of HCOONa.

observed within 8 h (Table 1, entries 10-11). Hence, the best optimised reaction conditions for chemoselective transfer hydrogenation of 1 mmol of benzylideneacetophenone were: PdNP: 1 mol % (5 mL stock solution in deionised water), HCOONa: 3 mmol, temperature: 100 °C, time: 8 h.

With these optimized reaction conditions in hand, we examined the reaction scope for the chemoselective reduction of α,β-unsaturated carbonyl compounds (Table 2). Introduction of the electron donating substituents on the aromatic ring of the model benzylideneacetophenone did not have any influence on the reaction course providing good yields with excellent selectivity towards olefinic bond (Table 2, entries 1-4) whereas, employing electron withdrawing groups such as chloro on aromatic ring gave good conversion of the desired product with slightly lower selectivity (Table 2, entries 5-6). We have not observed dehalogenation of these substrates under the optimised reaction condition. Furthermore, Benzylacetone was also provided excellent conversion and selectivity towards desired product (Table 2, entry 7). It is noteworthy to mention that heterocyclic enones such as furan and thiophene in the arene ring showed excellent yield and selectivity of the desired product (Table 2, entries 8-9).

Developed protocol was successfully applied to aliphatic cyclic enones like 5,5-dimethylcyclohex-2-enone and cyclohexenone providing desired yield and selectivity (Table 2, entries 10-11). Further, substrate scope extension were demonstrated on employing various functional groups such as esters, aldehydes, amides and α,β-unsaturated nitrile for chemoselective hydrogenation of olefinic bond (Table 2, entries 12-15). It is notable that aromatic enoate, amide and nitrile provided excellent yield of corresponding products with 100 % selectivity. Furthermore, the multiple bonds were also selectively reduced to the corresponding 1,4 adduct by adding excess of hydrogen source (Table 2, entry 16).

Our next step led us to engage PdNPs for recyclability study since nanoparticles offer reuse of precious palladium metal. It was observed that PdNPs were successfully recycled up to five conjugative cycles giving moderate to excellent conversion and chemoselectivity of the desired product. Further we have checked the morphology of reused (4th run) palladium nanoparticles by FEG-SEM analysis and we observed that the morphology of PdNPs remains same (FEG-SEM image of 4th run, see the ESI†).

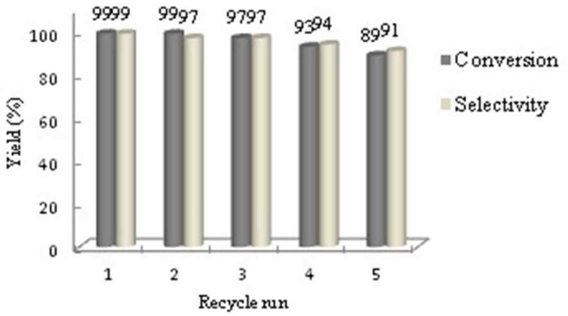


Figure 4 Recyclability of PdNPs in aqueous medium

Reaction conditions: benzylideneacetophenone (1 mmol), HCOONa (3 mmol), PdNPs (1 mol % in 5 mL deionised water), temperature (100 ºC). Conversion and selectivity determined by GC and GC-MS analysis.

Conclusions

In summary, we have developed a highly chemoselective ligand free catalytic system for transfer hydrogenation of α,β-unsaturated carbonyl compounds by PdNPs in aqueous reaction medium. The palladium nanoparticles offered reduction of wide variety of α,β-unsaturated carbonyl compounds such as carbonyls, esters, amides and nitriles with good to excellent conversion and chemoselectivity. The PdNPs were effectively recycled up to five consecutive cycles with appreciable conversion and selectivity. The use of PdNPs as a highly efficient catalyst for 1,4-reduction of α,β-unsaturated carbonyl compound under transfer hydrogenation condition in aqueous media adds credit towards advance of greener methodology for hydrogenation reaction.

Experimental Section

Experimental procedure for chemoselective conjugate reduction of α,β-unsaturated carbonyl

In a 5 mL stock solution of 1 mol % PdNPs were suspended in water, 1 mmol of corresponding α,β-unsaturated carbonyl compound and 3 mmol of HCOONa were added and the reaction mixture was stirred at 100 °C for 8 h. The progress of the reaction was monitored using thin layer chromatography (TLC) and GC analysis (Perkin Elmer, Clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm). On completion, the products were extracted with ethyl acetate, dried over Na_2SO_4 and the solvent was evaporated under vacuum. The obtained crude product was then purified by column chromatography using silica gel, (100-200 mesh size,) with petroleum ether/ethyl acetate (PE-EtOAc, 95:05) as eluent to afford pure product. All the products are well known in literature and were confirmed by ^1H NMR (Varian Mercury, 400 MHz NMR Spectrometer), ^{13}C NMR spectra (101 MHz), GC-MS (Shimadzu GC-MS QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10 °C/min. rise.) and IR (Perkin-Elmer FT-IR) spectroscopic techniques.

Recyclability study

The reaction was carried out as mentioned above in typical experimental procedure. After completion of reaction, the reaction mixture was cooled to room temperature and the product was extracted in ethyl acetate. The aqueous layer containing PdNPs was then used for further catalyst recyclability experiment and it was observed that the PdNPs could be reused up to five consecutive cycles affording good conversion with appreciable chemoselectivity.

Acknowledgment

The authors (D. B. Bagal) express gratitude towards University Grant Commission, India (UGC-SAP) for providing Research Fellowship.

Notes and references

1 E. Keinan and N. Greenspoon, *J. Am. Chem. Soc.* 1986, **108**, 7314; H. Lee, M. An, *Tetrahedron Lett.* 2003, **44**, 2775.

2 G. Neri, L. Mercadante, A. Visco and S. Galvagno, *Catal. Lett*. 1994, **29**, 379.

3 (a) G.Neri, L.Mercadante, A. Visco and S. Galvagno, *Catal. Lett.,* 1994, **29**, 379; (b) H. Lee and M. An, *Tetrahedron Lett.,* 2003, **44**, 2775; (c) A. Stolle, T. Gallert, C. Schmo¨ger and B. Ondruschka, *RSC Adv.*, 2013, **3**, 2112.

4 J. A. VanAllan, G. A. Reynolds and T. H. Regan, *J. Org. Chem*., 1967, **32**, 1897.

5 (a) M.-M. Wang, L. He, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, *Green Chem*., 2011, **13**, 602; (b) E. J. Corey and C. J. Helal, *Tetrahedron Lett.* 1995, **36**, 9153; (c) T. Ohkuma, H. Ooka, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.* 1995, **117**, 10417; (d) T. Ohkuma, H. Ikehira, T. Ikariya and R. Noyori, *Synlett* 1997, 467; (e) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.* 1998, **120**, 13529; (f) K. Mashima, T. Akutagawa, X. Zhang, H. Takaya, T. Taketomi, H. Kumobayashi and S. Akutagawa, *J. Organomet. Chem.* 1992, **428**, 213; (g) P. D. de Koning, M. Jackson and I. C. Lennon, *Org. Process Res. Dev.* 2006, **10**, 1054.

6 (a) K. Ahlford, J. Lind, L. Maeler and H. Adolfsson, *Green Chem.,* 2008, **10**, 832; (b) A. M. Kalsin , T. A. Peganova, V. V. Novikov, A. I. Zhamoytina, L. Gonsalvi, and M. Peruzzini, *Chem. Eur. J.* 2014, **20**, 846; (c) A. Zoran, Y. Sasson, *J. Mol. Catal.,* 1984, **26**, 321; (d) R. A. W. Johnstone and A. H. Wilby, *Chem. Rev.* 1985, **85**, 129; (e) G. Brieger and T. J. Nestrick, *Chemical Reviews.* 1974, **74**, 567.

7 (a) A. Sharma, V. Kumar and A. K. Sinha, *Adv. Synth. Catal*., 2006, **348**, 354; (b) E. Keinan and N. Greenspoon, *J. Am. Chem. Soc*., 1986, **108**, 7314; (c) H. Otsuka, E. Shirakawa and T. Hayashi, *Chem. Commun*., 2007, 1819; (d) M. L. Kantam, T. Parsharamulu and S. V. Manorama, *J. Mol. Catal. A: Chem*., 2012, **365**, 115; (e) Z. Baan, Z. Finta, G. Keglevich and I. Hermecz, *Tetrahedron Lett*., 2005, **46**, 6203; (f) A. mori, Y. Miyakawa, E. Ohashi and T. Haga, *Org. Lett.,* 2006, **8**, 3279.

8 (a) Y. Himeda, N. Onozawa-Komatsuzaki, S. Miyazawa, H. Sugihara, T. Hirose and K. Kasuga, *Chem.-Eur. J*., 2008, **14**, 11076; (b) Wei-Jing Lu, Yun-Wei Chen and Xue-Long Hou, *Angew. Chem., Int. Ed.,* 2008, **47**, 10133; (c) S. Sakaguchi, T. Yamaga and Y. Ishii, *J. Org. Chem*., 2001, **66**, 4710; (d) J. Blum, Y. Sasson and S. Iflah, *Tetrahedron Lett.,* 1972, **13**, 1015.

9 (a) X. Li, L. Li, Y. Tang, L. Zhong, L. Cun, J. Zhu, J. Liao and J. Deng, *J. Org. Chem.* 2010, **75**, 2981; (b) Z. Baan, Z. Finta, G. Keglevich and I. Hermecz, *Green Chem.,* 2009, **11**, 1937.

10 (a) Y. Sasson and J. Blum, *Tetrahedron Lett.* 1971, **12**, 2167; (b) Y. Sasson and J. Blum, *J. Org. Chem*. 1975, **40**, 1887; (c) G. Descotes and D. Sinou, *Tetrahedron Lett.* 1976, **17**, 4083; (d) T. Doi, T. Fukuyama, J. Horiguchi, T. Okamura and I. Ryu, *Synlett.* 2006, 721; (e) C. Mebi, R. Nair and B. Frost, *J. Organometallics*, 2007, **26**, 429.

11 (a) A. Kosal and B. Ashfeld, *Org. Lett*. 2010, **12**, 44; (b) E. Keinan and D. Perez, *J. Org. Chem.* 1987, 52, 2576; (c) D. Hays, M.Scholl and G. Fu, *J. Org. Chem.* 1996, **61**, 6751.

12 M. L. Kantam, R. Kishore, J. Yadav, M. Sudhakar and A. Venugopal, *Adv. Synth. Catal.,* 2012, **354**, 663.

13 S. Ganji, S. Mutyala, C. K. P. Neeli, K. Seetha, R. Rao and D. R. Burri, *RSC Adv*., 2013, **3**, 11533.

14 B. Ding, Z. Zhang, Y. Liu, M. Sugiya, T. Imamoto and W. Zhang, *Ogr. Lett.,* 2013, **15**, 3690.

15 (a) S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka and T. Teratani, *Langmuir,* 2010, **26**, 6230; (b) M. Moreno, J. Francisco, J. Jasinski and F. Zamborini, *J. Am. Chem. Soc.* 2011, **133**, 4389; (c) V. Budarin, J. Clark, R. Luque, D. Macquarrie and R. White, *Green Chem*., 2008,**10**, 382; (d) S. Kundu, K. Wang, S. Lau and H. Liang, *J. Nanopart. Res.* 2010, **12**, 2799.

16 (a) N. Yan, C. Xiao and Y. Kou, *Coord. Chem. Rev.,* 2010, **254**, 1179; (b) D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem. Int. Ed.* 2005, **44**, 7852.

17 (a) Y. Huang, Z. Zheng, T. Liu, J. Lü, Z. Lin, H. Li and R. Cao, *Catal. Commun.* 2011, **14**, 27; (b) Y. Huang, S. Gao, T. Liu, J. Lu, X. Lin, H. Li and R. Cao, *ChemPlusChem*, 2012, **77**, 106; (c) Y. Huang, Z. Lin and R. Cao, *Chem. Eur. J.,* 2011, **17**, 12706; (d) Y. Huang, S. Liu, Z. Lin, W. Li, X. Li and R. Cao, *J. Catal.* 2012, **292**, 111; (e) D. Ganapathy and G. Sekar, *Catal. Commun.,* 2013, **39**, 50; (f) J.

Durand, E. Teuma, F.Malbose, Y. Kihu and M. Gomez, *Catal. Commun*. 2008, **9**, 273; (g) J. Athilakshmi, S. Ramanathan, D. K. Chand, *Tetrahedron Lett.* 2008, **49**, 5286; (h) S. Gao, N. Zhao, M. Shu and S. Che, *Appl. Catal. A Gen.* 2010, **388**, 196; (i) H. Li, L. Wang, M. Yang and Y. Qi, *Catal. Commun*. 2012, **17**, 179; (j) P. K. Mandali and D. K. Chand, *Catal. Commun*. 2013, **31**, 16; (k) M. Beller, H. Fischer, K. Kuhlein, C.P. Reisinger and W.A. Herrmann, *J. Organomet. Chem.* 1996, **520**, 257; (l) J. Huang, T. Jiang, B. Han, H. Gao, Y. Chang, G. Zhao and W. Wu, *Chem. Commun.,* 2003, 1654.

18 (a) M. D. Bhor, M. J. Bhanushali, N. S. Nandurkar and B. M. Bhanage, *Catal. Commun*., 2007, **8**, 2064; (b) D. B. Bagal, R. A. Watile, M. V. Khedkar, K. P. Dhake and B. M. Bhanage, *Catal. Sci. Technol*., 2012, **2,** 354; (c) D. B. Bagal, Z. S. Qureshi, K. P. Dhake, S. R. Khan and B. M. Bhanage, *Green Chem*., 2011, **13**, 1490.

19 A. B. Patil, S. R. Lanke, K. M. Deshmukh, A. B. Pandit, B. M. Bhanage, *Materials Letters,* 2012, **79**, 1.