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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

## Palladium on Manganese ferrite: an efficient catalyst for one pot synthesis of primary amides from iodobenzene.

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

DOI: 10.1039/b000000x

Amidation of aryl halide in one pot is reported using Pd-MnFe<sub>2</sub>O<sub>4</sub> as a catalyst. The catalyst was characterized by various techniques such as XRD, FEG-SEM, EDS, TEM, BET surface area and ICP AES. K<sub>4</sub>[Fe(CN)<sub>6</sub>] is used as non toxic cyanation reagent for in situ generation of benzonitrile and hydrolyzed as soon as it formed. The catalyst was found to be efficient and can be used for several cycles without loss in activity. Moderate to good yield of primary amides was obtained.

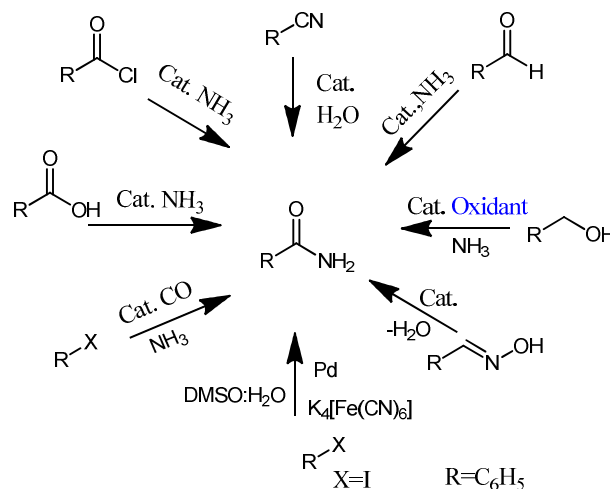
### 1. Introduction.

Primary amides are the most important functionality in pharmaceuticals, natural products, agrochemicals and biologically active molecules<sup>1-3</sup>. Generally, primary amides are synthesized either by reaction of carboxylic acid or its derivative with ammonia or its equivalent<sup>4</sup>. They are also synthesized by different methodologies such as catalytic rearrangement of aldoximes<sup>6</sup>, reaction of aldehydes with ammonia<sup>7</sup>, oxidation of benzylic alcohols in presence of ammonia<sup>8</sup> and catalytic oxidation of benzyl amines<sup>9</sup>. Aminocarbonylation of aryl halide by using carbon monoxide and ammonia or ammonia equivalent is also reported as the efficient method for the synthesis of primary amides. However, this process involves handling of toxic gas and reduces its use at kilogram level<sup>5</sup>. Aryl halides with ammonia in presence of metal carbonyls also have been used for the synthesis of primary amides, but it leads to release of toxic carbon monoxide gas and also the metal carbonyl complexes are volatile and unstable<sup>10</sup>. Hydration of nitriles is an atom economical process and numbers of catalytic methods have been developed for nitrile synthesis<sup>11</sup>. Hence preparation of nitriles as an intermediate for amide synthesis is of great importance. Nitriles are prepared by reaction of aryl halides with various nitrile sources such as alkali cyanide, CuCN, TMSCN and K<sub>4</sub>[Fe(CN)<sub>6</sub>] salt in presence of transition metal catalyst. Among these K<sub>4</sub>[Fe(CN)<sub>6</sub>] is used as a less toxic and cheaper cyanide source for cyanation of aryl halides<sup>12</sup>.

Recently oxidation of benzyl amine to primary amide by using OMS-2 catalyst was reported<sup>9c</sup>. However, the reaction requires very high pressure (6 bars) and temperature (160°C) and also gives side products, where as we have reported general synthesis of primary amides at mild reaction conditions using magnetically retrievable catalyst.

Magnetically separable catalyst has attracted much attention in the area of heterogeneous catalyst as it is easily separated by external magnet and can be used several times without losing its activity<sup>13</sup>. Super paramagnetic materials, spinel ferrites MFe<sub>2</sub>O<sub>4</sub> (M= Ni, Co, Zn,) are one of the important advance materials used

in drug delivery and biomedical applications such as MRI<sup>14</sup>. Besides this, they are also found to be good support for transition metal catalysts<sup>15</sup>. In particular, palladium supported on super paramagnetic material is the most important heterogeneous catalyst as it offers high surface area and easy separation. In continuation of our work with metal nano particles supported on super paramagnetic material<sup>15b</sup>, herein we report palladium nanoparticles (PdNPs) supported on MnFe<sub>2</sub>O<sub>4</sub> and its application in one pot synthesis of primary amides



Our Approach

Fig.1 General synthesis of primary amide.

Manganese ferrite (MnFe<sub>2</sub>O<sub>4</sub>) nano crystals possess higher magnetization as compared to magnetite, CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> nanoparticles<sup>16</sup>. Here we have carried out the tandem synthesis of primary amide from iodobenzene via in situ generation of benzonitrile in presence of DMSO: H<sub>2</sub>O solvent system using Pd nano particles supported on MnFe<sub>2</sub>O<sub>4</sub>. This is the first report of the application of the heterogeneous catalyst for the synthesis of primary amide and that too using nontoxic nitrile source

$K_4[Fe(CN)_6]$ . Very good yields of the desired products were obtained.

## 2. Experimental

### 2.1 Catalyst preparation.

Catalyst was prepared by using ultrasound assisted coprecipitation method.  $FeCl_3 \cdot 6H_2O$  (9.5 mmol, 50 mL) and  $MnCl_2 \cdot 4H_2O$  (4.4 mmol, 50 mL) solutions were added in 250 mL round bottom flask followed by addition of 0.5 g KCl and  $PdCl_2$  (60 mg). This mixture was placed in ultrasound bath for 5 min. Then pH of this mixture was adjusted at 12 by adding 3N NaOH followed by heating at 60 °C for 30 min. The obtained catalyst was filtered and washed with distilled water several times and then by ethanol to remove water. The catalyst was dried under vacuum at 60 °C for 24 h, and subsequently at 200°C for 4h.

### 2.2 Characterization of material

The as synthesized catalyst was characterized by various techniques such as X-ray diffraction (XRD), Field emission gun Scanning electron microscopy (FEG-SEM), Transmission electron microscopy (TEM), FTIR, ICP-AES analysis, BET surface area. The XRD analysis was performed on Shimadzu XRD 2400 instrument using  $Cu K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with scanning rate 2 degree per minute. TEM analysis was performed over PHILIPS 2200 instrument. FEG-SEM analysis was performed on TESCAN MIRA Instrument. The energy dispersive X-ray spectral analysis (EDS) image was recorded with an Oxford instrument at 10 kV. Beam intensity was kept high to get good response by the detector. Inductively coupled plasma Atomic Absorption spectrometry (ICP AES) analysis was performed on ARCOS from M/s. Spectro, Germany. GC analysis is performed over PerkinElmer Clarus 480 instrument. GC-MS Spectra recorded over Shimadzu QP-2010 Instrument.  $^1H$  and  $^{13}C$  NMR spectra's were recorded on Agilent 400MHz and 100MHz instrument respectively.

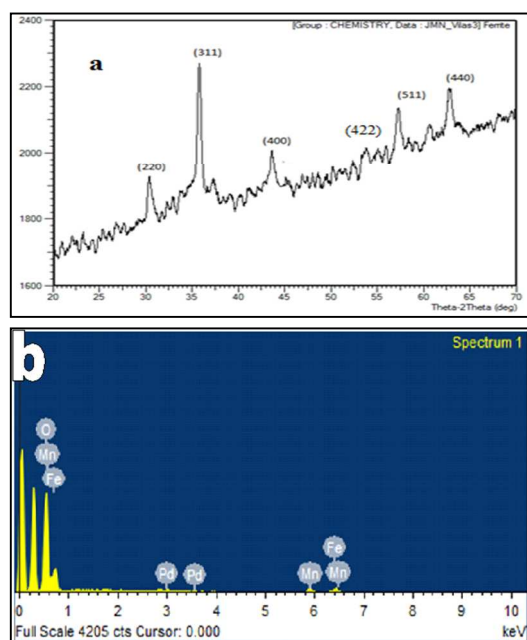


Fig.2 a) XRD and b) EDS analysis of  $Pd-MnFe_2O_4$

## 3. Results and Discussion

XRD analysis showed peak at  $2\theta = 30.1, 35.14, 43.41, 54.601, 57.0671$  and  $63.6651$  which represent the Bragg reflections from the (220), (311), (400), (422), (511) and (440) planes respectively. The crystalline data matches with the JCPDS Card No. (74-2403). Palladium peaks at 40, 46  $\theta$  values were not observed because of the low loading of the palladium (Fig 2a). Displacing value from XRD and TEM SEAD pattern is same and found to be  $2\text{ \AA}$ . (Fig. 3 c and d)

The elemental analysis of  $Pd-MnFe_2O_4$  was confirmed by EDS analysis as shown in (fig.2 b). The distribution of elements in  $Pd-MnFe_2O_4$  was  $Mn = 11.45\%$ ,  $Fe = 28.15\%$ ,  $O = 59.31\%$  and  $Pd = 1.09\%$ .

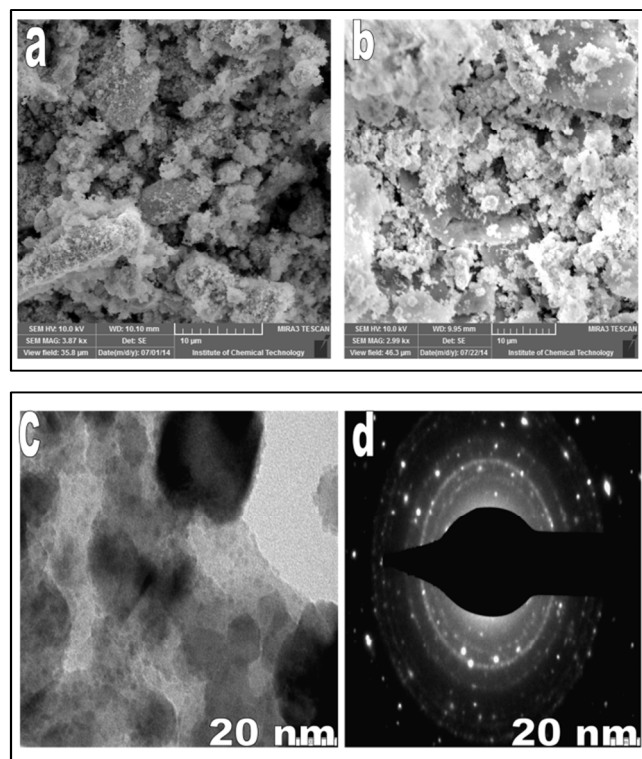


Fig.3 FEG-SEM image a) fresh and b) reused catalyst after fifth cycle. c) TEM image of catalyst and d) SEAD pattern.

FEG-SEM analysis shows highly crystalline morphology of the catalyst. (Fig. 3 c)

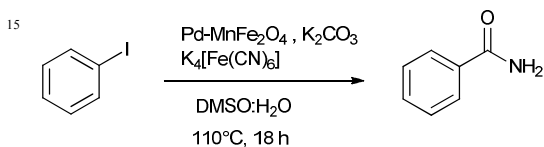
The TEM image of  $Pd-MnFe_2O_4$  NPs. (Fig.3 c) clearly indicates that NPs are uniform in size with average particle size less than 45 nm. This is in accordance with the average crystallite size obtained by using the Debye-Scherrer equation. The image also exhibits that the Pd NPs on  $MnFe_2O_4$  are well dispersed. Pd NPs size ranges from 2-10 nm.

From the  $N_2$  adsorption-desorption isotherm of  $Pd-MnFe_2O_4$  NPs, the BET surface area of the particles was found to be  $24.9346 \text{ m}^2/\text{g}$  and the adsorption average pore width was  $315 \text{ \AA}$ . Single point surface area at  $P/P_0 = 0.254238207$ :  $24.5190 \text{ m}^2/\text{g}$  (Fig.2 Supporting Information)

Reaction of iodobenzene with  $K_4[Fe(CN)_6]$  was treated as a

model reaction and various reaction parameters were optimized for this reaction. Initially (1 mmol) of iodobenzene was treated with 0.25 mmol of  $K_4[Fe(CN)_6]$  in the presence of Pd-MnFe<sub>2</sub>O<sub>4</sub> catalyst (30 mg, 1mol% Pd), K<sub>2</sub>CO<sub>3</sub> as a base in DMF:H<sub>2</sub>O (1:1) solvent system, at 100°C, which offered 58 % yield of benzamide (Table 1, entry 1) Series of experiments were performed to optimize the various reaction parameters such as catalyst loading, solvent, base and temperature of the reaction.

Loading of the catalyst was also the important parameter and it was found that 1 mmol of the catalyst was enough to achieve the maximum yield of the desired product (Table 1 entry 4). Solvent study was the important part for this transformation. Various solvent systems such as DMF:H<sub>2</sub>O, DMSO:H<sub>2</sub>O and NMP:H<sub>2</sub>O were used out of which



**Scheme 1.** One pot synthesis of amide from iodobenzene

**Table 1. Optimization of reaction parameters<sup>a</sup>**

Entry	Pd-MnFe <sub>2</sub> O <sub>4</sub> (mol %)	Base	Solvent: H <sub>2</sub> O	Temperature °C	Yield <sup>b</sup> %
1	0.5	K <sub>2</sub> CO <sub>3</sub>	DMF:H <sub>2</sub> O(1:1)	100	58
2	0.5	K <sub>2</sub> CO <sub>3</sub>	NMP:H <sub>2</sub> O(1:1)	100	64
3	0.5	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(1:1)	100	70
4	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(1:1)	100	78
5	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	100	84
6	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	88
7	2	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	88
8	3	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	88
9	1	Cs <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	74
10	1	TEA	DMSO:H <sub>2</sub> O(2:1)	110	trace
11	1	DBU	DMSO:H <sub>2</sub> O(2:1)	110	trace
12	1	KOH	DMSO:H <sub>2</sub> O(2:1)	110	20
13	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	90	19
14	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	120	91
15	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	140	90
16	1	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	110	-
17	1	K <sub>2</sub> CO <sub>3</sub>	DMSO	110	-*
18	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	90 <sup>c</sup>
19	1	K <sub>2</sub> CO <sub>3</sub>	DMSO:H <sub>2</sub> O(2:1)	110	90 <sup>d</sup>

<sup>a</sup>Reaction conditions: Aryl halide (1mmole), K<sub>4</sub>[Fe(CN)<sub>6</sub>] (0.25 mmole), Time 12h, base (1.2 mmole), <sup>b</sup>isolated yield., <sup>c</sup> time 18 h. <sup>d</sup> 24 h,

\*benzonitrile 92%

DMSO:H<sub>2</sub>O (2:1) was found to be the most suitable solvent system for this transformation (Table 1 entry 5). When reaction was carried out in DMSO solvent only, benzonitrile was formed (Table 1 entry 17). Iodobenzene was in situ converted to benzonitrile by the cyanating reagent K<sub>4</sub>[Fe(CN)<sub>6</sub>] which immediately gets hydrated to benzamide in the presence of water.

The reaction was also carried out with various inorganic and organic bases such as TEA, DBU, K<sub>2</sub>CO<sub>3</sub>, KOH and Cs<sub>2</sub>CO<sub>3</sub>, out of which K<sub>2</sub>CO<sub>3</sub> was found to be the most efficient base giving maximum yield of the benzamide (Table 1 entry 8). The reaction was also carried out at various temperatures under optimized

reaction conditions. The product yield increased dramatically from 19% to 90% when temperature increased from 90°C to 110°C whereas beyond 110°C no significant increase in the product yield with increase in temperature was observed (Table 1 entry 13-15)

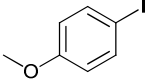
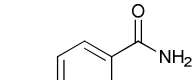
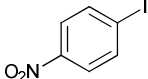
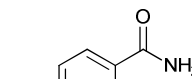
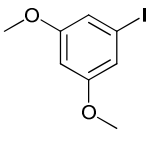
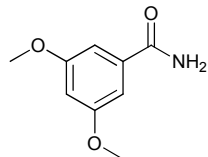
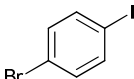
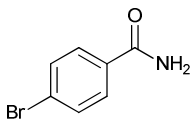
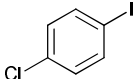
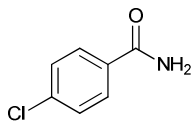
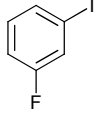
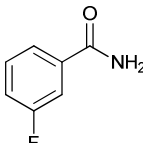

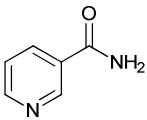
We also studied the effect of concentration of K<sub>4</sub>[Fe(CN)<sub>6</sub>] salt on the product yield by increasing the amount from 0.1 mmol to 0.25 mmol. Conversion of aryl halide to benzonitrile was 100% at 0.25 mmol concentration of K<sub>4</sub>[Fe(CN)<sub>6</sub>]. The reaction was also carried out at various time intervals and 100% conversion was obtained in 18 h. For optimized reaction TON and <sup>†</sup>TOF for amidation of iodobenzene was found to be 90 and 5 h<sup>-1</sup>.

The applicability of the protocol was examined for various substituted aryl iodides (Table 2). It was found that electron rich substrate gave very good yield of the desired product.

**Table 2.** One pot synthesis of primary amides from aryl iodides<sup>a</sup>.

Entry	Iodobenzene	Amide	Yield
1			90
2			20
3			-
4			88
5			90
6			80
7			88
8			90
9			88



10			90
11			78
12			84
13			84
14			88
15			85
16			81

<sup>a</sup>Reaction conditions: Aryl halide (1mmole),  $K_4[Fe(CN)_6]$  (0.25 mmole), 12h, base (1.2 mmole), Pd-MnFe<sub>2</sub>O<sub>4</sub> (30 mg, 1mol % Pd) <sup>b</sup>isolated yield.

In case of p-NO<sub>2</sub> iodobenzene electron withdrawing effect was more prominent giving moderate yield of the desired products. However, in m-Nitro iodobenzene the yield was increased due to minimum electron withdrawing effect. Results are summarized in (Table 2. entry 6 and 12).

Donating substituents at ortho positions were well tolerated giving good yield of the corresponding primary amides. We further studied amidation of bromobenzene as well as chlorobenzene and observed that bromobenzene gave only 20% yield of the desired product where as chlorobenzene was unreactive with optimized reaction conditions (Table 2 entry 2 and 3). Heteroaryl iodide also gave good yield of corresponding amide (Table 2 entry 16).

### Heterogeneous test for the catalyst

We also examined the heterogeneous nature of the catalyst by hot filtration test. The catalyst was separated from reaction mass after half of the reaction time and the filtrate was stirred for required time under same reaction conditions. The reaction did not

proceed further, which indicated that there is no leaching of palladium during the reaction. We also carried out the ICP AES analysis to test the recyclability of the catalyst for first and fifth cycles which showed that the palladium leaching was below detectable level (0.01 ppm).

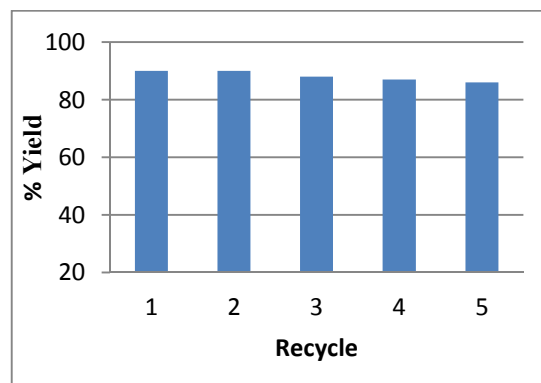


Fig. 4. Recycle study of the catalyst.

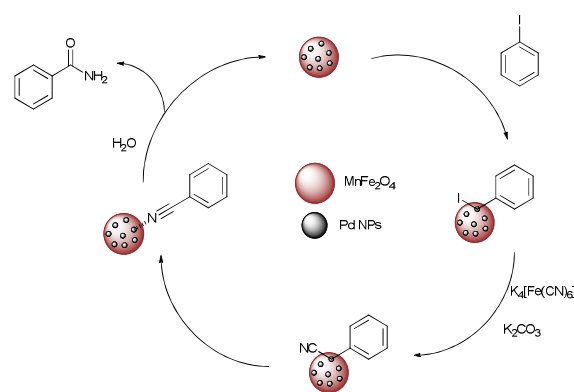


Fig. 5 Plausible Mechanism of the reaction.

Plausible mechanism suggests that iodobenzene is oxidatively added to the catalyst and then in presence of  $K_4[Fe(CN)_6]$  salt gives benzonitrile which subsequently get hydrolyzed in presence of water and catalyst to give primary amide.

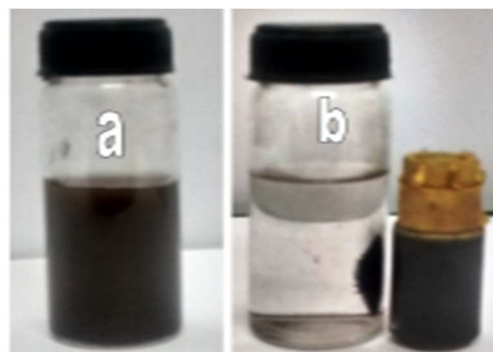


Fig. 6 Magnetic separation of the catalyst a) before and b) after applying external magnet.

## Conclusions

In summary, we have developed the simple and practically applicable protocol for the synthesis of primary amides from aryl iodides. Pd-MnFe<sub>2</sub>O<sub>4</sub> is the first heterogeneous catalyst for such transformation. Catalyst was found to be efficient for the transformation of iodobenzenes to respective amides. K<sub>4</sub>[Fe(CN)<sub>6</sub>] was used as the non toxic cyanating reagent and in situ generated benzonitrile was hydrated as soon as it forms. The catalyst can be retrieved using external magnet and reused up to five consecutive cycles without much loss in its activity.

## Acknowledgements

The authors are very thankful to the UGC-SAP, New Delhi, India for awarding the fellowship.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available:  
<sup>‡</sup> Electronic Supplementary Information (ESI) available: [Experimental procedure, Characterization of the catalyst, Mass and <sup>1</sup>H NMR spectrum of representative compounds are given]. See DOI: 10.1039/b000000x/  
<sup>‡</sup> TOF = [mol of product / (mol catalyst X h)].
- G. Arthur. The Amide Linkage: Selected Structural Aspects in Chemistry, Biochemistry, and Materials Science; Wiley-Interscience, 2000.
  - S. Budavari, The Merck Index, Merck, Rahway, USA, 11<sup>th</sup> edn, 1989
  - V. R. Pattabiraman, J. W. Bode, *Nature.*, 480, 2011,471.
  - (a) G. G. Arzoumanidis, F. C. Rauch, *J. Org. Chem.*, 1981 **46**, 3930–3932(b) C. L. Allen., J. M. Williams, *J. Chem. Soc. Rev.*, 2011, **40**, 3405–3415; (c) E. Valeur, M. Bradley, *Chem. Soc. Rev.* 2009, **38**, 606–631. (d) H. Lundberg, F. Tinnis, N. Selander and H. Adolffson, *Chem. Soc. Rev.*, 2014, **43**, 2714
  - (a) P. G. Alsabeh, M. Stradiotto, H. Neumann, M. Beller, *Adv. Synth. Catal.*, 2012, **354**, 3065–3070; (b) X.-F. Wu, H. Neumann, M. Beller, *Chem. Asian J.*, 2010, **5**, 2168–2172; (c) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Eur. J.*, 2010, **16**, 9750–9753; (d) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Eur. J.*, 2012, **18**, 419–422; (e) X.-F. Wu, J. Schranck, H. Neumann, M. Beller, *ChemCatChem.*, 2012, **4**, 69–71. (f) T. Xu, H. Alper, *Tetrahedron Lett.*, 2013, **54**, 5496–5499. (g) S. T. Gadge, B.M. Bhanage, *Synlett.*, 2014, **25**, 85 – 88
  - (a) A. Martinez-Asencio, M. Yus, D. J. Ramon. *Tetrahedron.*, 2012, **68**, 3948 – 3951. (b) F. Li, P. Qu, J. Ma; X. Zou, C. Sun, *ChemCatChem.*, 2013, **5**, 2178 – 2182. (c) N. A. Owston., A. J. Parker, J. M. Williams, *Org. Lett.*, 2007, **9**, 3599 – 3601. (d) C. Sun, P. Qu, F. Li, *Cat. Sci. and Tech.*, 2014, **4**, 988 - 996
  - (a) U. B. Patil, A. S. Singh, J. M. Nagarkar, *RSC Advances.*, 2014, **4**, 1102 – 1106. (b) Md. A. Ali, T. Punniyamurthy, *Adv. Synth. Catal.*, 2010, **352**, 288 – 292.
  - (a) K. Yamaguchi, H. Kobayashi, T. Oishi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2012, **51**, 544–547; (b) K. Yamaguchi, H. Kobayashi, Y. Wang, T. Oishi, Y. Ogasawara and N. Mizuno, *Catal. Sci. Technol.*, 2013, **3**, 318–327; (c) R. Nie, J. Shi, S. Xia, L. Shen, P. Chen, Z. Hou and F. Xiao, *J. Mater. Chem.*, 2012, **22**, 18115–18115; (d) R. Ohmura, M. Takahata and H. Togo, *Tetrahedron Lett.*, 2010, **51**, 4378–4381; (e) R. Das and D. Chakraborty, *Catal. Commun.*, 2012, **26**, 48–53; (f) X. -Q. Li, W. -K. Wang, Y. -X. Han and C. Zhang, *Adv. Synth. Catal.*, 2010, **352**, 2588–2598.
  - (a) X. -F. Wu, C. B. Bheeter, H. Neumann, P. H. Dixneuf and M. Beller, *Chem. Commun.*, 2012, **48**, 12237–12239; (b) J. W. Kim, K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2008, **47**, 9249–9251; (c) Y. Wang, H. Kobayashi, K. Yamaguchi and N. Mizuno, *Chem. Commun.*, 2012, **48**, 2642–2644
  - (a) W. Ren, M. Yamane, *J. Org. Chem.*, 2010, **75**, 8410 – 8415. (b) W. Ren, M. Yamane, *J. Org. Chem.*, 2010, **75**, 3017 – 3020.

- (a) J. Mauger, T. Nagasawa, H. Yamada *Tetrahedron.*, 1989, **45**, 1347 – 1354 (b) A. Goto, K. Endo, S. Saito, *Angew. Chemie – Int. Ed.*, 2008, **47**, 3607 – 3609. (c) R.S. Ramon., N. Marion, S. P. Nolan, *Chem. - A Eur. J.*, 2009, **15**, 8695 – 8697 (d) M. Muranaka., I. Hyodo., W. Okumura, T. Oshiki, *Cat. Today.*, 2011, **164**, 552 – 555 (e) E. Bolyog-Nagy, A. Udvardy, F. Joo., A. Katho, *Tetrahedron Lett.*, 2014, **55**, 3615 – 3617 (f) S. Kumar, P. Das, *New J. Chem.*, 2013, **37**, 2987 – 2990. (g) V. Polshettiwar, R.S. Varma, *Chem. - A Eur. J.*, 2009, **15**, 1582 – 1586 (h) T. Hirano, K. Uehara., K. Kamata, N. Mizuno, *J. Am. Chem. Soc.*, 2012, **134**, 6425 – 6433. (i) Nippon Shokubai Co. Ltd Patent: JP2005/170821 A, 2005. (j) Y. Wang., F. Wang., Q. Song, Q. Xin.; S. Xu, J. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 1506 – 1515. (k) K-T. Liu, M.-H. Shih, H.-W. Huang., C.-J. Hu, *Synthesis.*, 1988, **9**, 715 – 717.
- (a) T. Schareina, A. Zapf, M. Beller, *Chem. Commun.*, 2004, **40**, 1388 (b) T. Schareina, R. Jackstell, T. Schulz, A. Zapf, A. Cotte, M. Gotta, M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 643 (c) J. Huiliang, J. Jianzhong, W. Huixian, C. Chun, *Catal. Lett.*, 2013 **143**, 1195–1199.
- (a) W. L. Choon, In.S. Lee *Nano Today.*, 2010 **5**, 412–434. (b) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J-M. Basset *Chem. Rev.*, 2011, **111**, 3036–3075. (c) A. H. Latham and M. E. Williams, *Acc. Chem. Res.*, 2008, **41**, 411–420. (d) S.A Sarode, J.M. Bhojane, J. M. Nagarkar, *Tetrahedron Lett.*, 2014 doi:10.1016/j.tetlet.2014.11.065. (e) R.S. Shelkar, S. H. Gund, J. M. Nagarkar. *RSC Advances.*, 2014 **4** 53387-53396.
- (a) J. Lu, S. Ma, J. Sun, C. Xia, C. Liu, Z. Wang, X. Zhao, F. Gao, Q. Gong, B. Song, X. Shuai, H. Ai, Z. G. G. *Biomaterials.*, 2009, **30**, 2919–2928.
- (a) K. K. Senapati, S. Roy, C. Borgohain, P. Phukan *J. Mol. Cat. A: Chem.*, 2012, **352**, 128– 134. (b) A. S. Singh, U. B. Patil, J. M. Nagarkar, *Cat. Comm.* 2013 **35** 11-16. (c) S. R. Borhade, S. B. Waghmode; *Ind. J. Chem.*, 2008, **47**, 1549-1554. (d) D. Wang, D. Astruc *Molecules.*, 2014, **19**, 4635-4653. (e) N. Baig, R. S. Verma. *Chem. Commun.*, 2013, **49**, 752-770. (f) V. Polshettiwar, R. S. Verma. *Org. Bimol. Chem.*, 2009, **7**, 37-40.
- (a) U.I. Tromsdorf, N.C. Bigall, M.G. Kaul, O.T. Bruns, M.S. Nikolic, B. Mollwitz *Nano Lett.*, 2007, **7**, 2422. (b) J.H. Lee, Y.M. Huh, Y. Jun, J. Seo, J. Jang, H.T. Song, *Nat. Med.*, 2007, **13**, 95.