RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2016, **6**, 106873

Green synthesis of primary, secondary, and tertiary amides through oxidative amidation of methyl groups with amine hydrochlorides over recyclable $CoFe_2O_4$ NPs†

Esmaiel Eidi and Mohammad Zaman Kassaee*

Received 19th August 2016
Accepted 19th October 2016

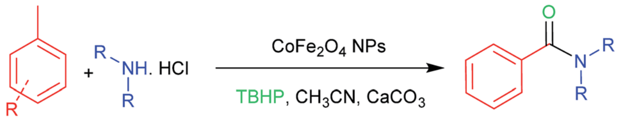
DOI: 10.1039/c6ra20902e

www.rsc.org/advances

A practical and efficient method is developed for efficient synthesis of a wide variety of 1°, 2°, and 3° amides through amidation of methylarenes with amine hydrochloride salts, over magnetic $CoFe_2O_4$ NPs as a recyclable nanocatalyst, and aqueous *tert*-butyl hydroperoxide as an oxidant. This economically sound amidation reaction is operationally straightforward and provides desired amides in good to excellent yields, under mild conditions.

Introduction

Developments in nanoscience and nanotechnology call for new synthetic approaches to final products with carefully tailored physicochemical properties. In recent years, nanoparticles as heterogeneous catalysts have attracted a great deal of attention because of their interesting structures and high catalytic activities.[1] From this aspect, bimetallic nanoparticles initiate better selectivity, catalytic activity and higher deactivation resistance compared to monometallic ones. Such improved properties can stem from synergetic electronic interactions between two different metal atoms in an individual nanoparticle. Catalytic activity of these systems depends mainly on the nature of the bimetallic, size and morphology of the particles.[2–4] Among the countless number of mixed metal oxides the nanostructured magnetic spinel type compounds MFe_2O_4 (M: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}) are attracting increasing attention due to their excellent magnetic performance and chemical stability.[5] In recent scenario much attention has been paid in the application of spinel and perovskite type metal oxides as catalysts for various organic transformations.[6–9] Cobalt ferrite ($CoFe_2O_4$) nanocrystals as a main category of bimetallic nanoparticles have properties, such as large surface area-to-volume ratio, high saturation magnetization, and size and shape dependent magnetic behavior.[10–16] Amides are one of the most important functional groups in contemporary chemistry and this motif plays a significant role in the synthesis of natural products, polymers, pharmaceuticals, and fine chemicals. Furthermore, it has been assessed that about 25% of all synthetic pharmaceutical drugs contain an amide unit. These properties have encouraged great challenges towards development of an efficient and practical protocol for the amide bond formation in synthetic chemistry. Amides are typically synthesized through condensation of carboxylic acids,[17] and their derivatives with amines.[18] Other methods for the synthesis of amides include, Staudinger reaction,[19] Schmidt reaction,[20] Beckmann rearrangement,[21] direct amide synthesis from amines and alcohols,[22] amidation of nitriles,[23] oxidative amidation of aldehydes,[24] and rearrangement of oximes.[25] However, most of these methods generate a large amount of wasteful byproducts and suffer from low atom efficiency. Thus, a more environmentally friendly, safe and highly atom-efficient method for the synthesis of amides is still needed. Direct oxidative amidation of methylarenes with amines is an attractive and economical method for synthesis of these compounds.[26] Here we report application of $CoFe_2O_4$ NPs, as a green, effective, clean, and recoverable magnetic nanocatalyst for the synthesis of important amides (Scheme 1).



Scheme 1 Oxidative amidation of methylarenes catalysed by $CoFe_2O_4$ NPs.

Results and discussion

In continuation of our previous work,[27] we reported the use of a heterogeneous cobalt ferrite nanocatalyst with high efficiency for the oxidative amidation of methylarenes with amine hydrochlorides. Cobalt ferrite was prepared and characterized *via* Fourier transform infrared (FT-IR), vibrating sample

---

Department of Chemistry, Tarbiat Modares University, P. O. Box 14155-4838, Tehran, Iran. E-mail: kassaeem@modares.ac.ir; drkassaee@yahoo.com; Fax: +98-21-88006544; Tel: +98-912-1000392

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra20902e

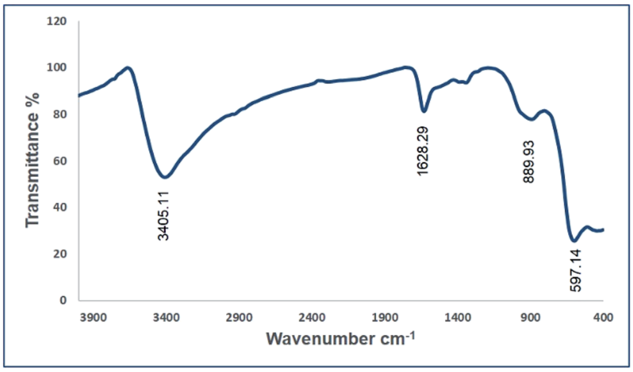


Fig. 1 FT-IR spectrum of $CoFe_2O_4$ NPs.

magnetometry (VSM), energy-dispersive spectrum (EDS), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and X-ray diffraction (XRD) analyses.

FT-IR spectroscopy

Among FT-IR peaks of $CoFe_2O_4$ are those at 597.14, 1628.29, and 3405.11 cm^{-1} (Fig. 1). The one at 597.54 cm^{-1} corresponds to the M–O tetrahedral site of the spinel structure, and shows the basic nature of the nanoparticles obtained. The broad bands at 3405.11 and 1628.29 cm^{-1} are assigned to OH stretching and bending vibrations of water, respectively.

X-ray diffraction

International Center for Diffraction Data PDF cards 3-864 and 22-1086, reveal that $CoFe_2O_4$ nanoparticles have cubic structure (Fig. 2).[28] The XRD pattern of the particles shows six different peaks at 2θ about 35.1°, 41.4°, 50.9°, 63.5°, 67.5° and 74.4° marked by their indices (220), (311), (400), (422), (511), and (440), respectively.

EDX

The structural composition of the catalyst is examined by EDX (Fig. 3). This analysis shows the elemental distribution of $CoFe_2O_4$ including Co and Fe.

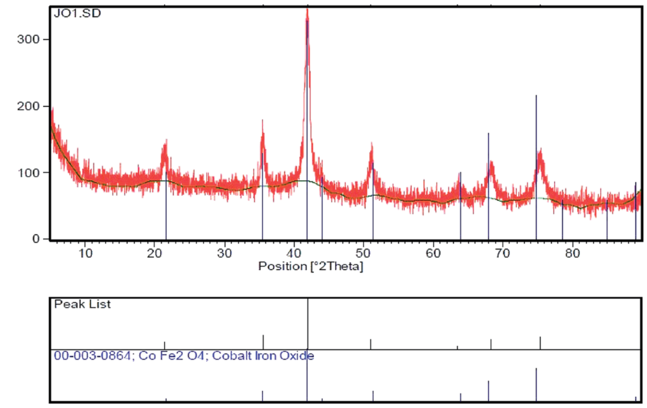


Fig. 2 XRD pattern of the catalyst $CoFe_2O_4$ NPs.

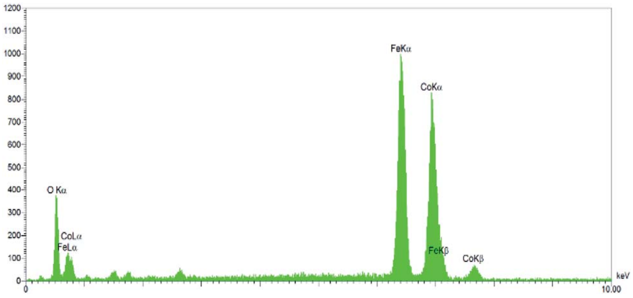


Fig. 3 Energy-dispersive spectrum (EDS) of $CoFe_2O_4$ NPs.

SEM

The size and morphology of $CoFe_2O_4$ NPs are estimated *via* SEM (Fig. 4). Uniformly dispersed spherical particles are observed, along with weak agglomerations.

VSM

Field-dependent magnetic measurements are performed on $CoFe_2O_4$ nanoparticles at room temperature, using VSM, in the range from +1 *T* to −1 *T* (Fig. 5). Room temperature specific magnetization (M) *vs.* applied magnetic field (H) curve measurements of the sample indicates a saturation magnetization value (M_s) of 17 emu g^{-1}.

Thermal analyses

In order to probe thermal stability, TGA analysis of $CoFe_2O_4$ NPs are carried out by heating NPs from room temperature to 900 °C at a rate of 10 °C min^{-1} (Fig. 6). The TGA pattern shows an initial weight loss attributed to water desorption at 100 °C. The slight weight loss below 350 °C may be due to dehydration of water or hydroxyl groups present on the surface of spinel structure, no further mass lose is detected up to 800 °C, which show the thermal stability of the catalyst.[29]

After characterization of $CoFe_2O_4$ nanocatalyst, its role as a heterogeneous nanocatalyst was evaluated for synthesis of *N*-benzylbenzamide through interaction of toluene with

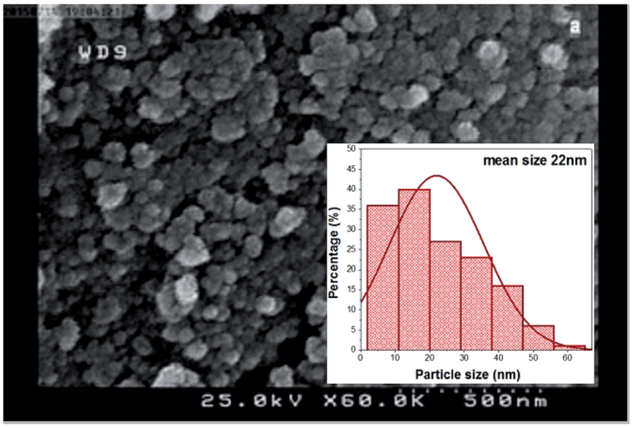


Fig. 4 SEM analysis of the catalyst $CoFe_2O_4$ NPs.

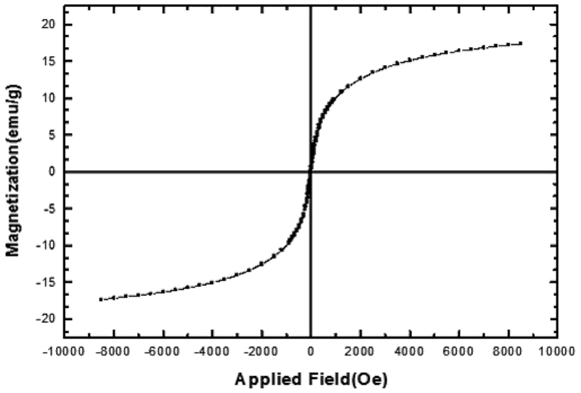


Fig. 5 Vibrating sample magnetometer (VSM) curve for $CoFe_2O_4$ NPs.

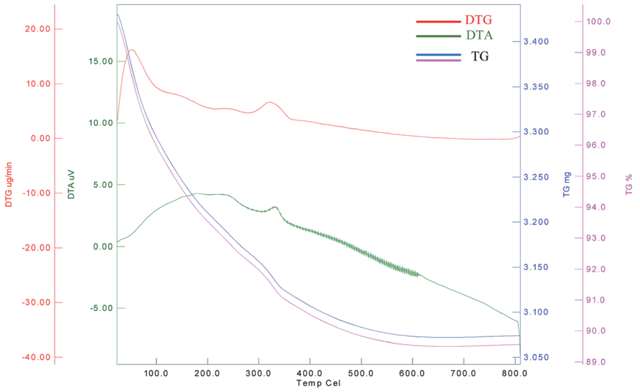
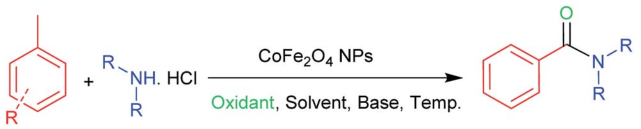


Fig. 6 TGA/DTA/DTG analysis of $CoFe_2O_4$ NPs.

Table 1 Optimization of the reaction conditions[a]



Entry	Cat. (mg)	Oxidant	Base	Solvent	Temp. (°C)	Yield[b] [%]
1	25	*t*-BuOOH	$CaCO_3$	CH_3CN	25	Trace
2	25	*t*-BuOOH	$CaCO_3$	CH_3CN	40	<10
3	25	*t*-BuOOH	$CaCO_3$	CH_3CN	60	37
4	20	*t*-BuOOH	$CaCO_3$	CH_3CN	70	58
5	25	*t*-BuOOH	$CaCO_3$	CH_3CN	70	74
6	20	*t*-BuOOH	$CaCO_3$	CH_3CN	80	90
7	25	*t*-BuOOH	$CaCO_3$	CH_3CN	80	90
8	20	*t*-BuOOH	$CaCO_3$	CH_3CN	90	77
9	15	*t*-BuOOH	$CaCO_3$	CH_3CN	80	73
10	20	*t*-BuOOH	$CaCO_3$	DMSO	80	55
11	20	*t*-BuOOH	$CaCO_3$	THF	80	32
12	20	*t*-BuOOH	$CaCO_3$	DMF	80	24
13	20	*t*-BuOOH	$CaCO_3$	CH_2Cl_2	80	20
14	20	*t*-BuOOH	Na_2CO_3	CH_3CN	80	64
15	20	*t*-BuOOH	K_2CO_3	CH_3CN	80	59
16	20	*t*-BuOOH	Cs_2CO_3	CH_3CN	80	50
17	20	*t*-BuOOH	Et_3N	CH_3CN	80	32
18	20	*m*-CPBA	$CaCO_3$	CH_3CN	80	14
19	20	H_2O_2	$CaCO_3$	CH_3CN	80	28
20	—	*t*-BuOOH	$CaCO_3$	CH_3CN	80	—
21	20	—	$CaCO_3$	CH_3CN	80	—

[a] Reaction conditions: toluene (1 mmol), benzyl amine hydrochloride salt (1.5 mmol), oxidant (6 equiv.), base (3 equiv.), solvent (2 mL), under Ar atmosphere, 9 h. [b] Isolated yields.

benzylamine hydrochloride salt, and employed it as a model reaction. Effects of solvents, oxidants, base, temperature, and amounts of catalyst on the reaction rate were probed under similar circumstances. At first, the model reaction studied with different amounts of catalyst (15, 20, 25 mg) in various temperature. After screening different mounts of catalyst, best result was obtained in the presence of 20 mg of catalyst. In order to probe the role of the solvents, the reaction was examined in various solvent such as, DMSO, THF, MeCN, CH_2Cl_2, and DMF. Among them, MeCN appeared to be the solvent of choice. In addition, we explored different oxidant sources and the best result was obtained with *tert*-butyl hydroperoxide (TBHP), while other oxidants were ineffective in giving the desired product. No product was observed in the absence of an oxidant. Also, experiments were carried out under similar conditions using different bases such as Cs_2CO_3, K_2CO_3 and Na_2CO_3. The best base among several others was $CaCO_3$. It is important to note that in the absence of the catalyst, only trace products were detected. Optimum conditions for this reaction were employment of 20 mg $CoFe_2O_4$ at 80 °C, in acetonitrile using $CaCO_3$ as the base and *t*-BuOOH as the oxidant (Table 1).

Subsequently, we investigated the substrate scope of this reaction under the established optimal conditions, and produced a wide range of primary, secondary and tertiary amides (Table 2). Generally, electron-donating substituents gave higher yields than their electron-withdrawing substituted counterparts. Encouraged by these promising results for the successful synthesis of primary and secondary amides, we extended the scope of this protocol for the formation of tertiary amides by carrying out reactions between methylarenes and secondary amines.

Based on these results and literature reports,[30] we propose a plausible free radical mechanism as shown in Scheme 2. Initially, Co^{2+} metal center catalysis the heterolytic cleavage of *tert*-butyl hydroperoxide to *tert*-butylperoxyl radical and a proton. The *tert*-butylperoxyl radical abstract a hydrogen from the toluene to give the benzyl radical intermediate (I). Subsequently, the benzaldehyde (II) is generated from the benzyl radical (I) in the presence of *tert*-butyl hydroperoxide and *tert*-butoxyl radical. The benzaldehyde can react with the free amine, generated *in situ* from the reaction of the amine salt with $CaCO_3$, to form a hemiaminal intermediate (III). Finally, the corresponding amide product is obtained by the same $CoFe_2O_4$–TBHP catalytic system. In the presence of a radical scavenger 2,6-di-*tert*-buty-4-methylphenol, completely stopped the oxidation, and no product was detected. It seems that the reactions proceed *via* the radical path. According to this, a free-radical mechanism is confirmed for oxidative amidation.

Reusability of the catalyst is evaluated under the reaction conditions described above for the model reaction. After

Table 2 Oxidative amidation of methylarenes with amine hydrochlorides in the presence of $CoFe_2O_4$ NPs[a]

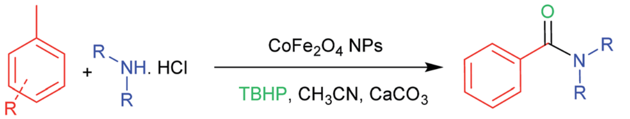
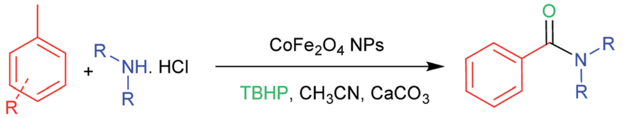
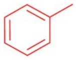
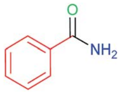
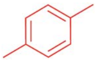
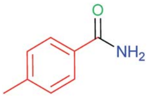
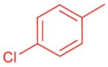
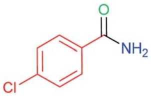
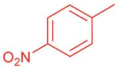
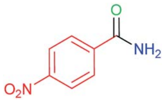
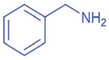
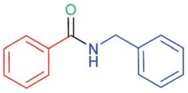
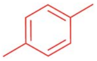
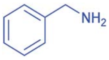
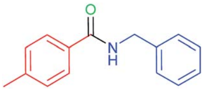
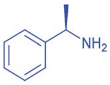
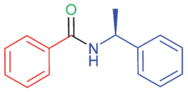
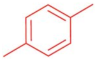
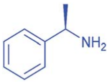
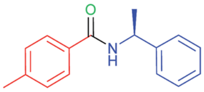
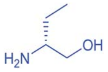
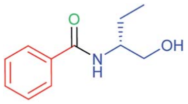
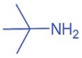
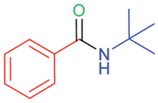
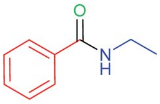
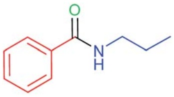
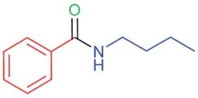
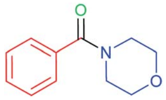
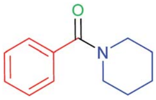
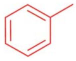
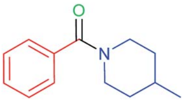
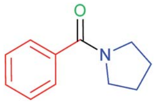
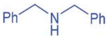
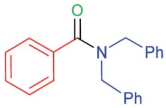
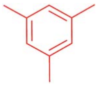
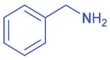
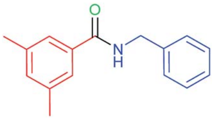
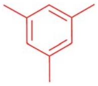
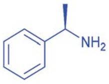
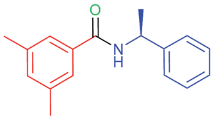
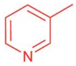
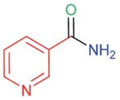
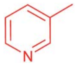
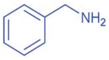
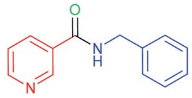
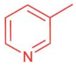
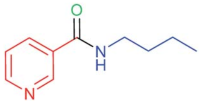


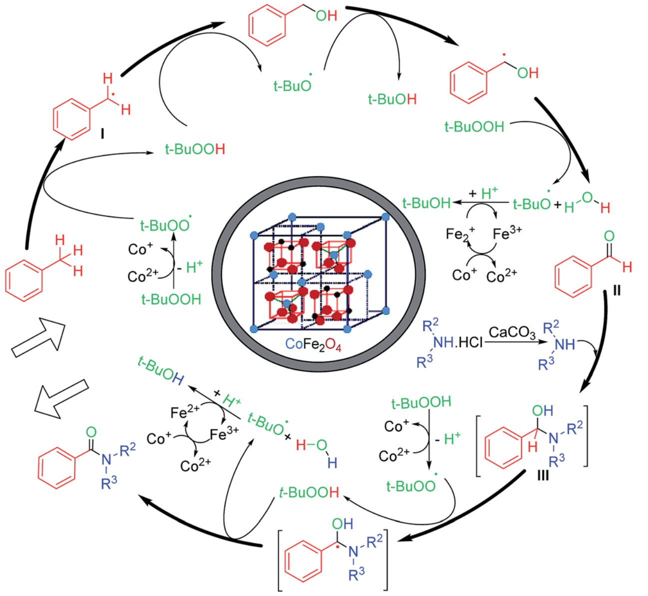
Table 2 (Contd.)



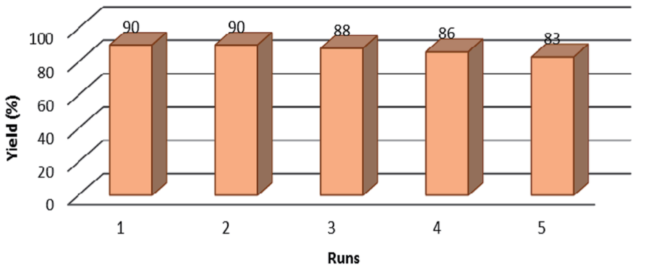
Entry	Methylarenes	Amine	Product	Yield[b] [%]
1		NH_3		78
2		NH_3		82
3		NH_3		76
4		NH_3		60
5				90
6				91
7				82
8				84
9				73
10				64
11				70
12				72
13				77
14				80
15				78
16				75
17				77
18				71
19				70
20				68
21		NH_3		53
22				55
23				46

[a] Reaction conditions: methylarenes (1 mmol), amine hydrochloride salt (1.5 mmol), CH_3CN (2 mL), $CaCO_3$ (3 equiv.), *t*-BuOOH (6 equiv.), catalyst (20 mg), 80 °C, under Ar atmosphere, 9 h. [b] Isolated yields.

completion of the reaction, the catalyst was easily recovered by applying a strong external permanent magnet, followed by washing with ethanol to remove the residual product(s). Then the recovered catalyst was dried under vacuum, and reused



Scheme 2 A plausible mechanism for catalytic oxidative amidation of methylarenes with amine hydrochloride salts over $CoFe_2O_4$ NPs.



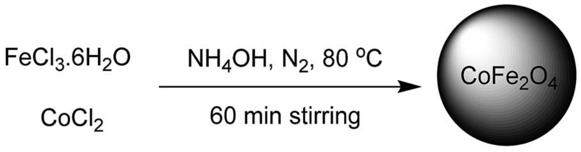
Scheme 3 Reusability of nanocatalyst in synthesis of *N*-benzylbenzamide.

directly for the next cycle without further treatment. The catalyst was used over five runs, and no obvious loss in the catalytic activity was observed (Scheme 3).

Experimental

General

All chemical reagents used in our experiments were purchased from Merck or Aldrich Chemical Company with high purity. All solvents were distilled, dried and purified using standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (DPX 500 MHz and DPX 125 MHz) in pure deuterated $CDCl_3$ solvent using tetramethylsilane (TMS) as an internal reference. FT-IR spectra were recorded using KBr pellets on a Nicolet IR-100 infrared spectrometer. The powder X-ray diffraction spectrum was recorded at room temperature using a Philips X-Pert 1710 diffractometer. The latter appeared with Co Kα ($\alpha = 1.79285$ Å) voltage: 40 kV, current: 40 mA and was in the range of 20–80° (2θ) with a scan speed of 0.02° per s. The particle morphology was examined by scanning electron microscopy using SEM (HITACHI S-4160) on gold coated samples. Magnetic properties were obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran).



Scheme 4 Preparation of magnetic $CoFe_2O_4$ nanocatalyst.

Preparation of magnetic $CoFe_2O_4$ nanoparticles (MNPs)

Magnetic $CoFe_2O_4$ nanoparticles were prepared by chemical co-precipitation chlorine salt of Fe^{3+} and Co^{2+} ions with a molar ratio of 2 : 1. Typically, $FeCl_3 \cdot 6H_2O$ (5.8 g, 0.02 mol) and $CoCl_2$ (1.3 g, 0.01 mol) were dissolved in 100 mL deionized water at 80 °C under N_2 atmosphere and vigorous stirring. Then, 10 mL of 25% NH_4OH was quickly injected into the reaction mixture in one portion. The addition of the base to the Co^{2+}/Fe^{3+} salt solution resulted in immediate formation of a black precipitate of MNPs. The reaction was continued for another 60 min and the mixture was cooled to room temperature. The black precipitate was washed with doubly warm distilled water (Scheme 4).

General procedure for direct amidation of methylarenes with amine hydrochloride salts

A mixture was made that consisted of catalyst (20 mg), an amine hydrochloride salt (1.5 mmol), $CaCO_3$ (3 equiv.), methylarenes (1 mmol), and *t*-BuOOH (70 wt% in H_2O, 6 equiv.), in CH_3CN (2 mL), under an argon atmosphere for appropriate time at 80 °C. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with EtOAc. The catalyst was separated using an external magnet, washed several times with EtOAc and dried under vacuum at room temperature to be ready for a later run. The mixture was extracted with EtOAc, then the combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to provide the desired amides.

Conclusions

This work demonstrates a novel and highly efficient methodology for the formation of amides from reaction of methylarenes with amine hydrochloride salts, and aqueous *tert*-butyl hydroperoxide as an oxidant using recyclable $CoFe_2O_4$ NPs. This protocol provides high yield, short reaction time, and operational simplicity, green and low cost procedure for the synthesis of all types of amides (primary, secondary and tertiary). The highlights of this work are the reusability and rather high efficiency of the synthesized nanocatalyst.

Acknowledgements

We acknowledge Tarbiat Modares University for partial support of this work.

Notes and references

1. (*a*) N. R. Shiju and V. V. Guliants, *Appl. Catal., A*, 2009, **356**, 1–17; (*b*) L. D. Pachón and G. Rothenberg, *Appl. Organomet. Chem.*, 2008, **22**, 288–299.
2. (*a*) I. Beletskaya and V. Tyurin, *Molecules*, 2010, **15**, 4792–4814; (*b*) B. P. S. Chauhan, R. Thekkathu, L. Prasanth, K. M. Mandal and K. Lewis, *Appl. Organomet. Chem.*, 2010, **24**, 222–228; (*c*) B. P. S. Chauhan, R. Sardar, U. Latif, M. Chauhan and W. Lamoreaux, *Acta Chim. Slov.*, 2005, **52**, 361–370.
3. N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, **22**, 1179–1201.
4. F. M. Moghaddam, G. Tavakoli and H. R. Rezvani, *Appl. Organomet. Chem.*, 2014, **28**, 750–755.
5. G. Bate, in *Magnetic Oxides Part 2*, ed. D. J. Craik, John Wiley & Sons, New York, 1975, pp. 705–707.
6. A. S. Reddy, C. S. Gopinath and S. Chilukuri, *J. Catal.*, 2006, **243**, 278–291.
7. A. H. de Morais Batista, F. S. Ramos, T. P. Braga, C. L. Lima, F. F. de Sousa, E. B. Barros, M. Josue Filho, A. S. de Oliveira, J. R. de Sousa and A. Valentini, *Appl. Catal., A*, 2010, **382**, 148–157.
8. K. Sreekumar, T. Mathew, B. M. Devassy, R. Rajgopal, R. Vetrivel and B. Rao, *Appl. Catal., A*, 2001, **205**, 11–18.
9. (*a*) A. S. Kulkarni and R. V. Jayaram, *Appl. Catal., A*, 2003, **252**, 225–230; (*b*) B. Baruwati, M. N. Nadagouda and R. S. Varma, *J. Phys. Chem. C*, 2008, **112**, 18399–18404.
10. Y. Wang, J. Park, B. Sun, H. Ahn and G. X. Wang, *Chem.–Asian J.*, 2012, **7**, 1940–1946.
11. D. Fritsch and C. Ederer, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 014406–014416.
12. R. Comes, H. X. Liu, M. Kholchov, R. Kasica, J. W. Lu and S. A. Wolf, *Nano Lett.*, 2012, **12**, 2367–2373.
13. R. S. Turtelli, G. V. Duong, W. Nunes, R. Grössinger and M. Knobel, *J. Magn. Magn. Mater.*, 2008, **320**, e339–e342.
14. B. Q. Liu, Q. F. Li, B. Zhang, Y. L. Cui, H. F. Chen, G. N. Chen and D. P. Tang, *Nanoscale*, 2011, **3**, 2220–2226.
15. H. X. Wu, G. Liu, X. Wang, J. M. Zhang, Y. Chen, J. L. Shi, H. Yang, H. Hu and S. P. Yang, *Acta Biomater.*, 2011, **7**, 3496–3504.
16. Y. D. Yang, S. Priya, Y. U. Wang, J. F. Li and D. Viehland, *J. Mater. Chem.*, 2009, **19**, 4998–5002.
17. (*a*) L. Perreux, A. Loupy and F. Volatron, *Tetrahedron*, 2002, **58**, 2155–2162; (*b*) C. L. Allen, A. R. Chhatwal and J. M. Williams, *Chem. Commun.*, 2012, **48**, 666–668.
18. E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606–631.
19. (*a*) E. Saxon and C. R. Bertozzi, *Science*, 2000, **287**, 2007–2010; (*b*) F. Damkaci and P. De Shong, *J. Am. Chem. Soc.*, 2003, **125**, 4408–4409; (*c*) Y. G. Gololobov and L. F. Kasukhin, *Tetrahedron*, 1992, **48**, 1353–1406.
20. (*a*) T. Ribelin, C. E. Katz, D. G. English, S. Smith, A. K. Manukyan, V. W. Day, B. Neuenswander, J. L. Poutsma and J. Aubé, *Angew. Chem., Int. Ed.*, 2008, **47**, 6233–6235; (*b*) S. Lang and J. Murphy, *Chem. Soc. Rev.*, 2006, **35**, 146–156.
21. (*a*) N. A. Owston, A. J. Parker and J. M. Williams, *Org. Lett.*, 2007, **9**, 3599–3601; (*b*) M. Hashimoto, Y. Obora, S. Sakaguchi and Y. Ishii, *J. Org. Chem.*, 2008, **73**, 2894–2897.
22. (*a*) C. Gunanathan, Y. B. David and D. Milstein, *Science*, 2007, **317**, 790–792; (*b*) P. C. Chiang, Y. Kim and J. W. Bode, *Chem. Commun.*, 2009, 4566–4568; (*c*) L. U. NordstrØm, H. Vogt and R. Madsen, *J. Am. Chem. Soc.*, 2008, **130**, 17672–17673; (*d*) M. Arefi, D. Saberi, M. Karimi and A. Heydari, *ACS Comb. Sci.*, 2015, **17**, 341–347; (*e*) S. C. Ghosh, J. S. Ngiam, A. M. Seayad, D. T. Tuan, C. W. Johannes and A. Chen, *Tetrahedron Lett.*, 2013, **54**, 4922–4925; (*f*) X. Wu, M. Sharif, A. Pews-Davtyan, P. Langer, K. Ayub and M. Beller, *Eur. J. Org. Chem.*, 2013, **2013**, 2783–2787.
23. (*a*) S.-I. Murahashi, T. Naota and E. Saito, *J. Am. Chem. Soc.*, 1986, **108**, 7846–7847; (*b*) C. L. Allen, A. A. Lapkin and J. M. J. Williams, *Tetrahedron Lett.*, 2009, **50**, 4262–4264.
24. (*a*) J. W. W. Chang, T. M. U. Ton, S. Tania, P. C. Taylor and P. W. H. Chan, *Chem. Commun.*, 2010, **46**, 922–924; (*b*) T. M. U. Ton, C. Tejo, S. Tania, J. W. W. Chang and P. W. H. Chan, *J. Org. Chem.*, 2011, **76**, 4894–4904; (*c*) S. C. Ghosh, J. S. Ngiam, C. L. Chai, A. M. Seayad, T. T. Dang and A. Chen, *Adv. Synth. Catal.*, 2012, **354**, 1407–1412; (*d*) S. C. Ghosh, J. S. Ngiam, A. M. Seayad, D. T. Tuan, C. L. Chai and A. Chen, *J. Org. Chem.*, 2012, **77**, 8007–8015; (*e*) K. S. Goh and C.-H. Tan, *RSC Adv.*, 2012, **2**, 5536–5538; (*f*) X. Liu and K. F. Jensen, *Green Chem.*, 2012, **14**, 1471–1474; (*g*) G.-L. Li, K. K.-Y. Kung and M.-K. Wong, *Chem. Commun.*, 2012, **48**, 4112–4114; (*h*) M. Zhu, K.-i. Fujita and R. Yamaguchi, *J. Org. Chem.*, 2012, **77**, 9102–9109.
25. (*a*) S. Park, Y. Choi, H. Han, S. H. Yang and S. Chang, *Chem. Commun.*, 2003, 1936–1937; (*b*) N. A. Owston, A. J. Parker and J. M. J. Williams, *Org. Lett.*, 2007, **9**, 73–75.
26. (*a*) J. B. Feng and X. F. Wu, *Appl. Organomet. Chem.*, 2015, **29**, 63–86; (*b*) T. Wang, L. Yuan, Z. Zhao, A. Shao, M. Gao, Y. Huang, F. Xiong, H. Zhang and J. Zhao, *Green Chem.*, 2015, **17**, 2741–2744; (*c*) Y. Huang, T. Chen, Q. Li, Y. Zhou and S.-F. Yin, *Org. Biomol. Chem.*, 2015, **13**, 7289–7293.
27. E. Eidi, M. Kassaee and Z. Nasresfahani, *Appl. Organomet. Chem.*, 2016, **30**, 561–565.
28. (*a*) X. B. Cao and L. Gu, *Nanotechnology*, 2005, **16**, 180–185; (*b*) T. Hyeon, Y. Chung, J. Park, S. S. Lee, Y. W. Kim and B. H. Park, *J. Phys. Chem. B*, 2002, **106**, 6831–6833; (*c*) S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273–279; (*d*) T. Prozorov, P. Palo, L. Wang, M. Nilsen-Hamilton, D. Jones, D. Orr, S. K. Mallapragada, B. Narasimhan, P. C. Canfield and R. Prozorov, *ACS Nano*, 2007, **1**, 228–233.
29. (*a*) J. K. Rajput and G. Kaur, *Chin. J. Catal.*, 2013, **34**, 1697–1704; (*b*) P. Sivakumar, R. Ramesh, A. Ramanand,

S. Ponnusamy and C. Muthamizhchelvan, *Mater. Res. Bull.*, 2011, **46**, 2204–2207.

30 (*a*) A. S. Kumar, B. Thulasiram, S. B. Laxmi, V. S. Rawat and B. Sreedhar, *Tetrahedron*, 2014, **70**, 6059–6067; (*b*) B. Ma, Z. Zhang, W. Song, X. Xue, Y. Yu, Z. Zhao and Y. Ding, *J. Mol. Catal. A: Chem.*, 2013, **368**, 152–158; (*c*) K. V. Rao, P. Rao, P. Nagaraju, P. S. Prasad and N. Lingaiah, *J. Mol. Catal. A: Chem.*, 2009, **303**, 84–89; (*d*) T. C. Mac Leod, M. V. Kirillova, A. J. Pombeiro, M. A. Schiavon and M. D. Assis, *Appl. Catal., A*, 2010, **372**, 191–198; (*e*) P. K. Tandon, M. Srivastava, S. Kumar and S. Singh, *J. Mol. Catal. A: Chem.*, 2009, **304**, 101–106.