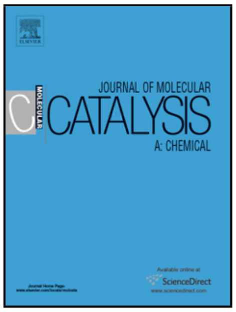


Title: Palladium Nanoparticles Supported on Magnetic Copper Ferrite Nanoparticles: The Synergistic Effect of Palladium and Copper for Cyanation of Aryl Halides with $K_4[Fe(CN)_6]$

Author: Mohammad Gholinejad Afsaneh Aminianfar

PII: S1381-1169(14)00484-1
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2014.10.029
Reference: MOLCAA 9331

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 10-9-2014
Revised date: 30-10-2014
Accepted date: 31-10-2014

Please cite this article as: M. Gholinejad, A. Aminianfar, Palladium Nanoparticles Supported on Magnetic Copper Ferrite Nanoparticles: The Synergistic Effect of Palladium and Copper for Cyanation of Aryl Halides with $K_4[Fe(CN)_6]$, *Journal of Molecular Catalysis A: Chemical* (2014), http://dx.doi.org/10.1016/j.molcata.2014.10.029

Palladium Nanoparticles Supported on Magnetic Copper Ferrite Nanoparticles: The Synergistic Effect of Palladium and Copper for Cyanation of Aryl Halides with $K_4[Fe(CN)_6]$

Mohammad Gholinejad [a*] Afsaneh Aminianfar [a]

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gava zang, Zanjan 45137-6731, Iran.

Email: gholinejad@iasbs.ac.ir

Abstract

In this paper, for the first time, palladium nanoparticles were supported on (3-aminopropyl)triethoxysilane-modified copper ferrite nanoparticles. The obtained catalyst was characterized using FT-IR, TEM, EDX, AAS, XRD, and TGA analyses. The prepared heterogeneous catalyst showed superior activity toward cyanation of aryl iodides and bromides with $K_4[Fe(CN)_6]$ compared to the Fe_3O_4 supported palladium nanoparticles, unfunctionalized $CuFe_2O_4$ nanoparticles, homogeneous $Pd(OAc)_2$, $CuCl_2$, and CuI catalysts. The heterogeneous and low Pd loading catalyst was recycled for four consecutive runs with small drops in catalytic activity.

Keywords: Magnetic, Palladium, Copper, Synergistic, Cyanation

1. Introduction

Aryl nitriles are important moieties of numerous biological, agrochemicals, pharmaceutical, and natural products [1,2]. The nitrile compounds can be easily converted into several important functional products such as acids, amides, aldehydes, ketones, and amines [3]. For more than a century, the traditional methods for the synthesis of aryl nitriles were the Rosenmund–von Braun [4-8], Sandmeyer and ammoxidation reactions [9-10]. However, ammoxidation reaction typically has performed under harsh reaction conditions, such as elevated temperatures (220-550 °C) and under high pressure conditions. Also, via the Rosenmund–von Braun and Sandmeyer methods, aryl iodides, bromides and aryl diazonium salts can be converted to aryl nitriles using stoichiometric amount of CuCN at high reaction temperature (150-250 °C) [3].

Over the last few years, in order to reduce the mentioned drawbacks and meet today's criteria of sustainable synthesis, different transition metal-catalyzed methodologies for the preparation of aryl nitriles from the reaction of aryl halide and cyanide sources have been reported. For this purpose, different catalysts such as palladium [11], copper [12-20], nickel [21], and rhodium [22] were developed. In addition, different metal-or metalloid-bound cyanide sources such as KCN [23-26], CuCN [4-10], NaCN [27-29], $Zn(CN)_2$ [30-36], TMSCN [37-38], and $K_4[Fe(CN)_6]$ [39-43] were employed for the cyanation of aryl compounds. Furthermore, in recent years extensive attention has been paid to using of nonmetallic organic cyanide sources such as acetone cyanohydrins, benzylthiocyanate, ammonium bicarbonate, formamide, malononitrile, benzyl nitrile, azobisisobutyronitrile, acetonitrile, and ammonium iodide-DMF [44]. Despite the low reactivity of $K_4[Fe(CN)_6]$ in comparison to the some of the other cyanide sources, $K_4[Fe(CN)_6]$ was known as a general, nontoxic, inexpensive, and easily handled cyanide source.

Copper catalyzed cyanation of aryl ioddies and bromides using $K_4[Fe(CN)_6]$ usually performed under harsh reaction condition such as high temperature or microwave heating conditions [12-20]. However, using palladium precatalysts for the cyanation of aryl halides affected this reaction to performed under mild reaction conditions in comparison to the copper precatalysts. Though the significant efficiency in some of the reported palladium catalyzed cyanation reactions, these reactions usually were performed under high loading of expensive palladium precatalysts in the presence of phosphane ligands under homogeneous reaction conditions [11]. In particular, phosphanes are excellent ligands for the stabilization of the palladium species. However, phosphanes are usually toxic, unrecoverable, thermally unstable, and their synthesis is difficult. On the other hand, less attention has been paid to use of heterogeneous palladium catalysts in the cyanation reaction of aryl halides.

Nowadays, bimetallic nanoparticles have been known as efficient catalysts for various catalytic reactions. The synergistic combination of two metals enhanced their catalytic performance, activity, selectivity, and stability in compared to corresponding monometallic catalysts [45]. In addition, mass decreasing of bimetallic catalyst relative to the individually using of metals in reactions such as Sonogashira in which usually a second metal is required, is other advantage of bimetallic catalysts [46].

Ferrites nanoparticles are important magnetic materials, which are used for various applications such as drug delivery, magneto-thermal therapy, microwave absorbent sensors, and as catalyst for many organic transformations [47]. In recent years, there has been growing interest in the application of copper ferrite nanoparticles as a recyclable catalyst in the different copper catalyzed organic reactions [48-60]. Very recently, we have introduced copper ferrite nanoparticles as an efficient catalyst for odorless carbon sulfur bond formation reactions [61].

In this context, for the first time, stabilization of palladium nanoparticles on (3-aminopropyl)triethoxysilane-modified copper ferrite nanoparticles is described. The new catalyst was successfully applied for the cyanation of aryl iodides and bromides under heterogeneous and low palladium loading conditions.

2. Experimental Section

2.1. General

All chemicals were purchased from Sigma-Aldrich, Acros and Merck and were used without further purification. Thin layer chromatography was carried out on silica gel 254 analytical sheets obtained from Fluka. Column chromatography was carried out on silica gel 60 Merck (230-240 mesh) in glass columns (2 or 3 cm diameter) using 15-30 grams of silica gel per one gram of the crude mixture. ^{1}H NMR spectra were recorded at 250 and 400 MHz and ^{13}C NMR were recorded at 100 MHz in $CDCl_3$ using TMS as internal standard. Thermogravimetric analysis (TGA) was conducted from room temperature to 600 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. FT-IR spectra were recorded on a Bruker Vector 22. X-ray diffraction (XRD) was recorded on Philips X'PertPro. Energy dispersive X-ray analysis (EDX) was obtained using Carl Zeiss □iGMA instrument. The structures of the prepared materials were observed by transmission electron microscopy (Philips CM-120).

2.2. Preparation of the catalyst

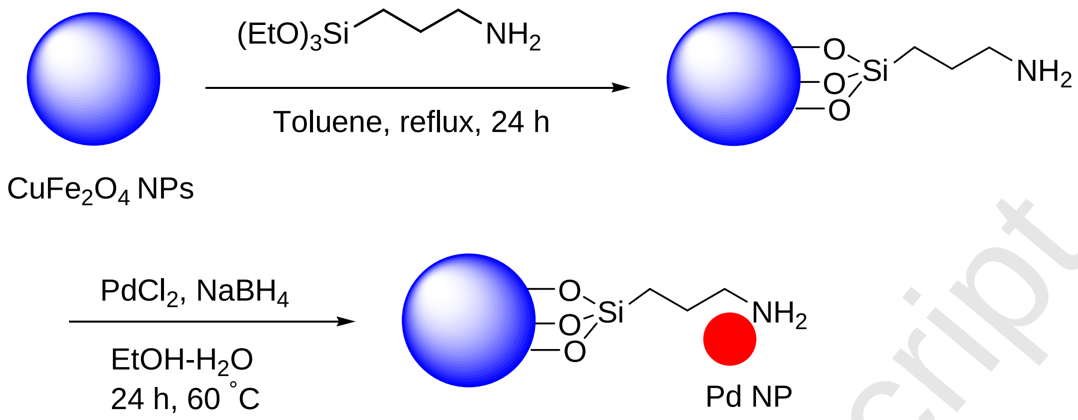
$CuFe_2O_4$ nanoparticles were synthesized by procedures described previously [90]. 500 mg of as-synthesized $CuFe_2O_4$ NPs were dispersed in 20 mL dry toluene for 30 min using ultrasound assistance. To the resulting solution, 2 mmol of 3-aminopropyltriethoxysilane was added and mixture was refluxed for 24 h under argon atmosphere. The (3-aminopropyl)triethoxysilane functionalized $CuFe_2O_4$ NPs was subjected to magnetic separation, and was washed sequentially with EtOH (3×20 mL) and dried under vacuum for 24 h. Then, 500 mg of functionalized $CuFe_2O_4$ NPs were dispersed in 20 mL EtOH for 30 min and to this solution, a solution of $PdCl_2$ (12.5 mg, 0.07 mmol) in 10 mL hot water was added. To the resulting mixture, solution of 1 mmol $NaBH_4$ in 5 mL water was added and the mixture was stirred for 12 h at room temperature. The solid catalyst was separated by external magnet, washed sequentially with EtOH (3×20 mL) and dried under vacuum for 24 h.

2.3. General procedure for the cyanation of aryl bromides and iodides using Pd@$CuFe_2O_4$ NPs

To a 10 mL glass tube aryl halide (1 mmol), K_4FeCN_6 (0.6 mmol, 220 mg), K_2CO_3 (1.5 mmol, 207 mg), catalyst (10 mg), and 2 mL DMF were added and mixture was stirred for appropriate reaction time at 120 °C under argon atmosphere. The progress of the reaction was monitored by GC analysis. After completion of the reaction, reaction mixture was washed with 5 mL water and crude product was isolated using dichloromethane (5 × 1 mL). Organic extracts were combined together, evaporated and purified by flash chromatography using hexane/EtOAc to give the desired aryl cyanide products.

3. Results and Discussion

$CuFe_2O_4$ nanoparticles were synthesized using $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ via conventional co-precipitation method without using any capping agent or surfactant [60]. Copper ferrite nanoparticles-supported palladium catalyst was synthesized according to the procedure summarized in Scheme 1.



Scheme 1. Synthesis of Copper ferrite nanoparticles-supported palladium nanoparticles Pd@$CuFe_2O_4$ NPs.

The loading of palladium in the catalyst was determined using atomic absorption spectroscopy (AAS) and a amount of 0.1 mmol.g^{-1} was obtained. Also, thermalgravimetric analysis showed three steps of weight losses and confirmed presence of supported organic functional group (0.72 mmol.g^{-1}) (Figure 1). The first weight loss occurred between 25 and 100 °C, with an observed weight loss of 3.36% related to the loss of H_2O. The second weight loss occurred between 100-200 °C which may be related to the physisorbed 3-aminopropyl)triethoxysilane group and third weight loss between 100-500 °C is related to the supported 3-aminopropyl)triethoxysilane organic group on $CuFe_2O_4$ NPs [62].

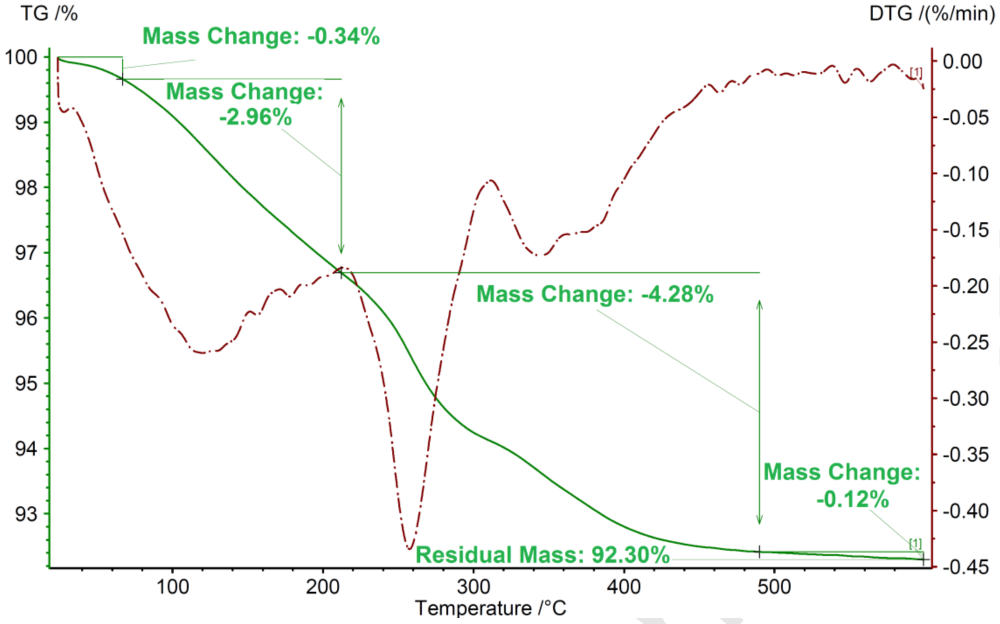


Figure 1. Thermogravimetric diagram of Pd@$CuFe_2O_4$ NPs

The presence of stretching mode for Fe-O band at 575 cm^{-1}, Cu-O at 438 cm^{-1} and the broad peak at 3432 cm^{-1} for surface O-H groups in FT-IR confirmed the structure of prepared copper ferrite nanoparticles. However, appearance of two new peaks at 585 cm^{-1} and 1008 cm^{-1} which may be related to the Fe-O-Si [63] and Cu-O-Si [64] bonds confirms the structure of Pd@$CuFe_2O_4$ catalyst (Figure 2).

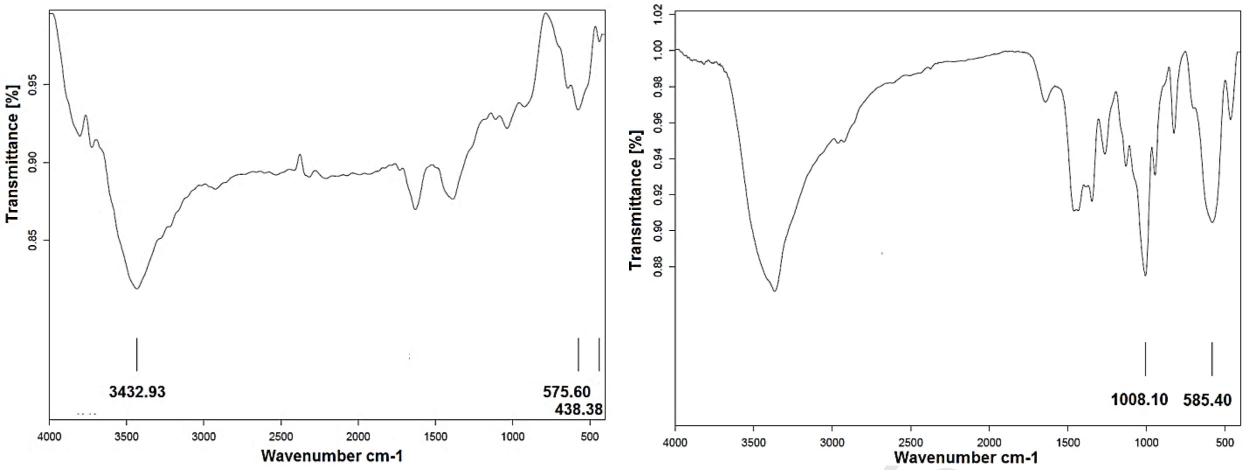
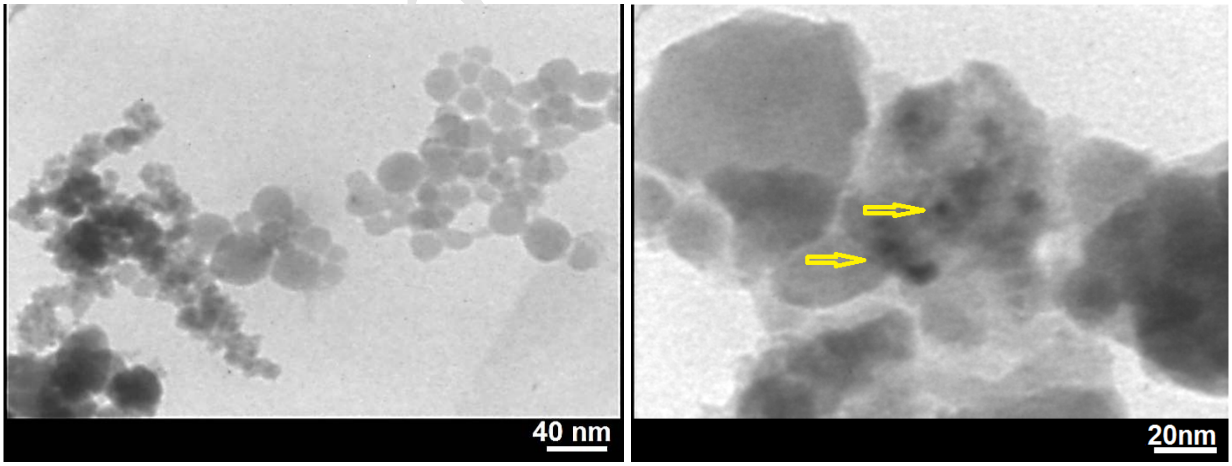


Figure 2. FT-IR spectrums of $CuFe_2O_4$NPs (left) and Pd@$CuFe_2O_4$ catalyst (right)

Figure 3 shows TEM image of Pd@$CuFe_2O_4$ catalyst, in which palladium nanoparticles with average size of 5-10 nm were assembled on 40-60 nm (3-aminopropyl)triethoxysilane functionalized copper ferrite nanoparticles. In addition, EDX (SEM) spectrum of catalyst showed the presence of palladium species in the catalyst (Figure 4).



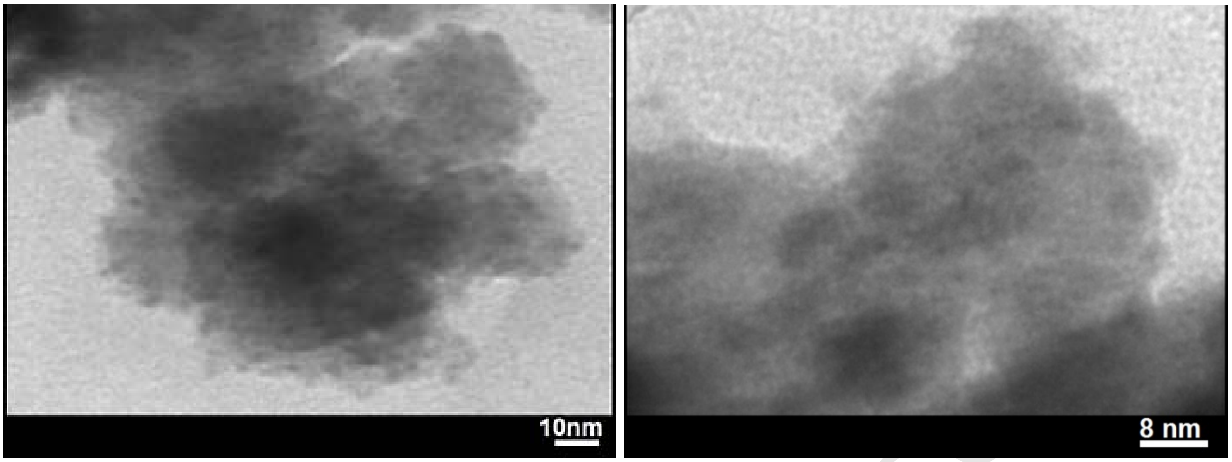


Figure 3. TEM images of Pd@$CuFe_2O_4$ NPs

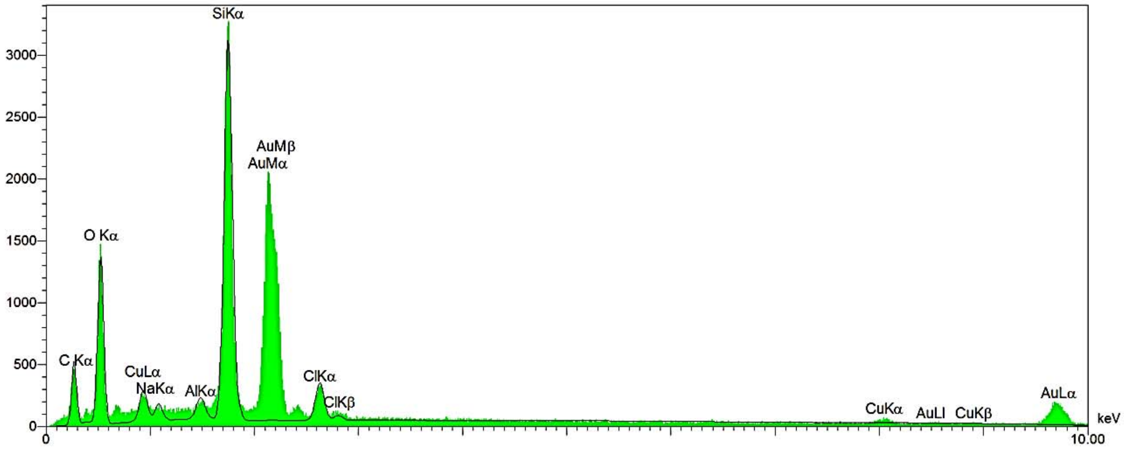


Figure 4. EDX spectrum of Pd@$CuFe_2O_4$ NPs

The X-ray diffraction (XRD) analysis of catalyst confirmed formation of catalyst by screening Bragg's reflections related to $CuFe_2O_4$ nanoparticles [62] in 2θ = 18.3, 30.3, 35.6, 57.1, 62.98 and Bragg's reflections related to palladium [65] in 2θ= 40.1, 46.7, 68.1.

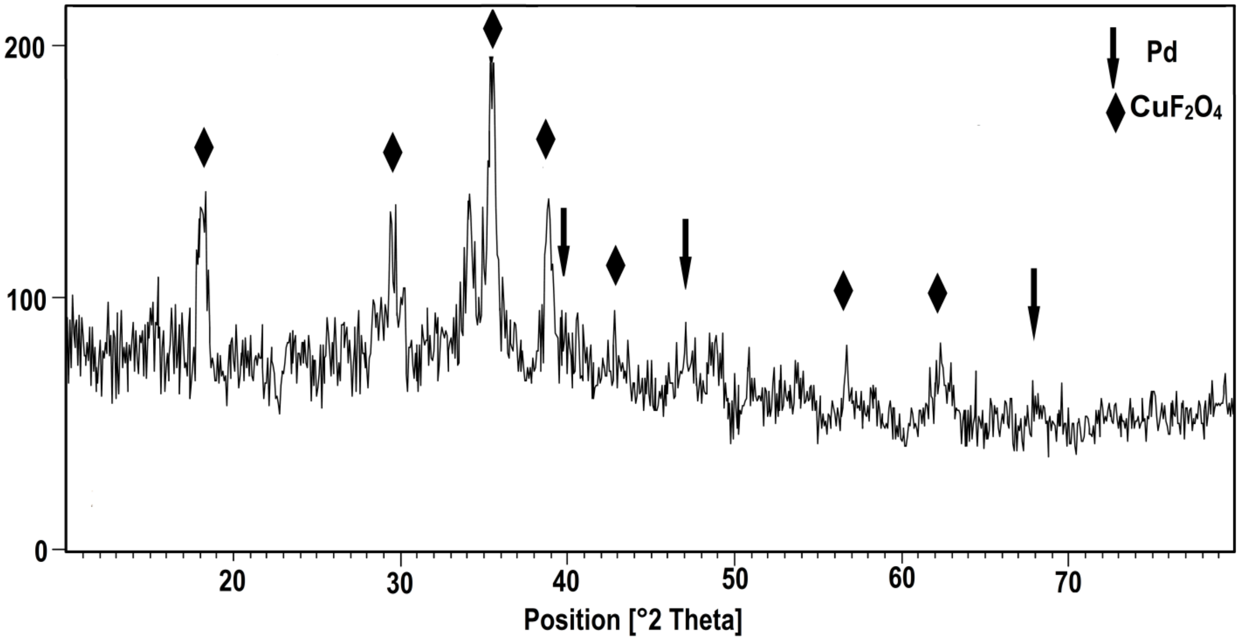
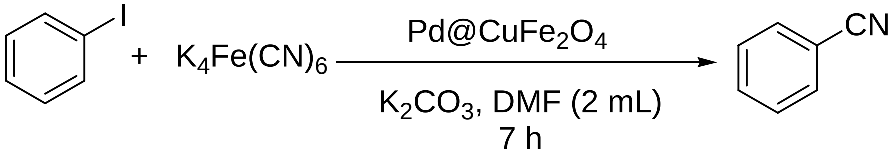


Figure 5. XRD pattern of the catalyst

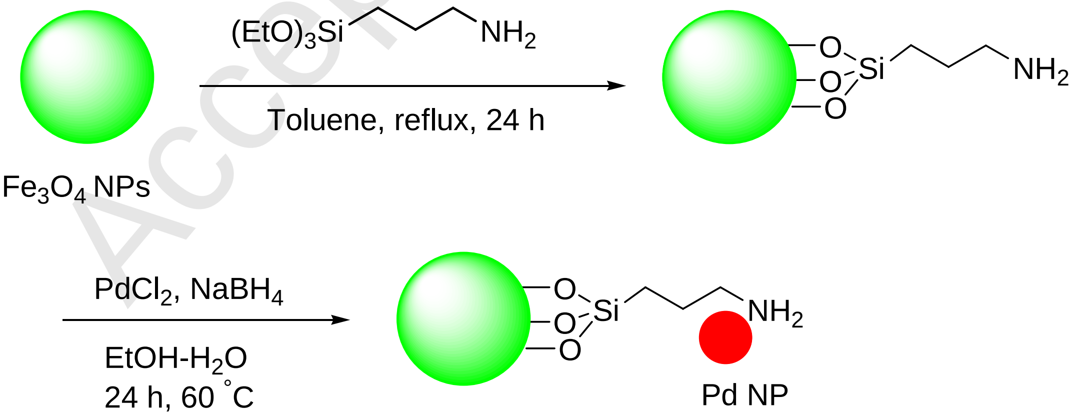
Hypothesizing the synergistic effect of the palladium and copper nanoparticles in the catalyst, cyanation reaction of iodobenzene with $K_4Fe(CN)_6$ in the presence of 10 mg catalyst (0.001 mmol Pd) and K_2CO_3 as a base in DMF at different temperatures was studied. The results showed that after 7 h reaction proceeded well at 120 °C and benzonitrile as the product was obtained in 97% GC yield (Table 1).

Table 1 Reaction of iodobenzene with $K_4Fe(CN)_6$ in the presence of catalyst at different temperatures



Entry	T (°C)	Yield%
1	100	72
2	110	89
3	120	97

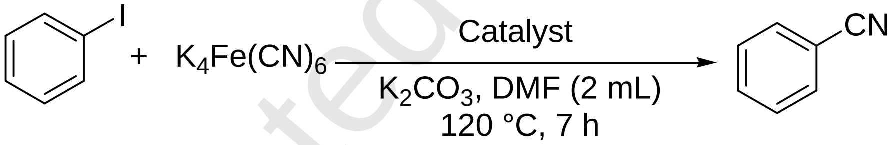
In order to demonstrate the synergistic effect between two metals, reaction of iodobenzene with $K_4Fe(CN)_6$ as a model reaction under different reaction conditions in the absence of Pd@$CuFe_2O_4$ was studied. First of all, palladium nanoparticles supported on Fe_3O_4 nanoparticles was prepared using similar method to preparation of Pd on $CuFe_2O_4$ to give Pd@Fe_3O_4 catalyst (scheme 2). AAS showed the amount of palladium on Fe_3O_4 nanoparticles was 0.12 mmol per gram which is approximately same as the Pd on $CuFe_2O_4$. Then, the obtained catalyst was tested for model reaction under similar optimized reaction conditions. However, GC analysis of the reaction after 7 h showed only 13% conversion of iodobenzene to benzonitrile (Table 2, entry 2).



Scheme 2. synthesis of Copper ferrite nanoparticles-supported palladium nanoparticles Pd@Fe_3O_4 NPs

Furthermore, reaction of iodobenzene with $K_4[Fe(CN)_6]$ in the presence of 10 mg unfunctionalized copper ferrite nanoparticles under optimized reaction conditions afforded only 6% GC yield for benzonitrile after 7 h (Table 2, entry 3). Also, the reaction of 1 mmol iodobenzene with $K_4Fe(CN)_6$ in the presence of 0.001 mmol $Pd(OAc)_2$, 1.5 mmol K_2CO_3 at 120 °C in DMF was investigated. After 7 h, 31% (GC) conversion of iodobenzene to benzonitrile was achived (Table 3, entry 4). The model reaction was also performed using 5 mol% of CuI or $CuCl_2$ under optimized reaction condition. However GC analysis of reaction showed only 4-5% production of benzonitrile (Table 3, entries 5 and 6). In addition, using 10 mg of unfunctionalized Fe_3O_4 NPs (containing 0.001 mmol Pd) as a catalyst for the reaction, gave trace amount of benzonitrile as the product (Table 3, entry 7).

Table 2 Reaction of iodobenzene with $K_4Fe(CN)_6$ in the presence of different catalysts



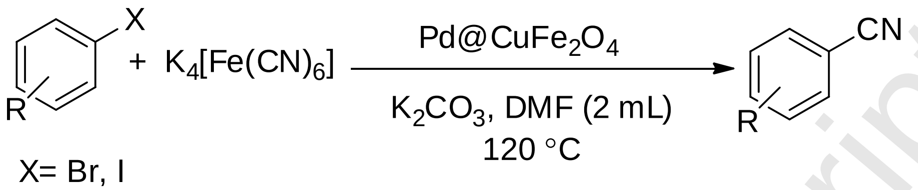
Entry	Catalyst	Yield%
1	Pd@$CuFe_2O_4$NPs (10 mg, containing 0.001 mmol Pd)	97
2	Pd@Fe_3O_4NPs (10 mg, containing 0.001 mmol Pd)	13
3	$CuFe_2O_4$NPs (10 mg)	6
4	$Pd(OAc)_2$ (0.001 mmol)	31
5	CuI (0.05 mmol)	4
6	$CuCl_2$ (0.05 mmol)	5
7	Fe_3O_4NPs (10 mg)	trace

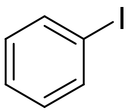
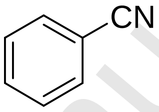
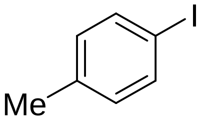
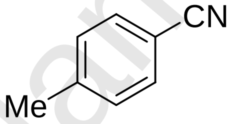
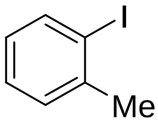
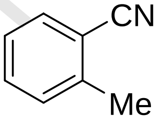
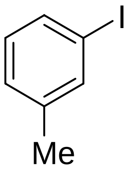
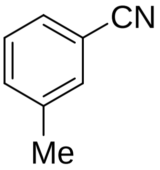
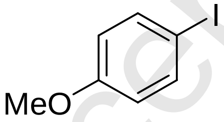
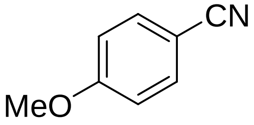
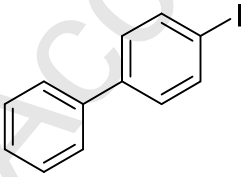
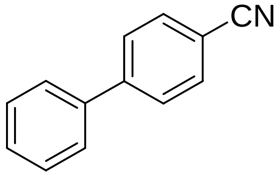
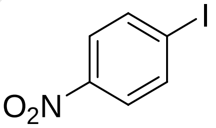
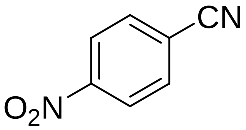
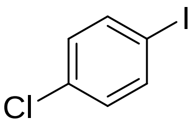
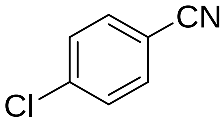
8	$Pd(OAc)_2$ (0.001 mmol) + CuI (0.05 mmol)	88
9	$Pd(OAc)_2$ (0.001 mmol) + $CuCl_2$ (0.05 mmol)	91
10	$Pd@Fe_3O_4$ (containing 0.001 mmol Pd) + $CuCl_2$(0.05 mmol)	82

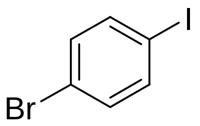
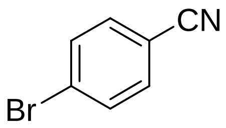
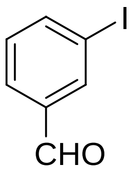
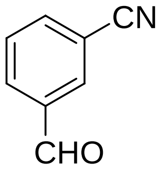
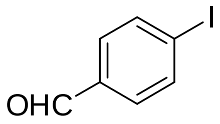
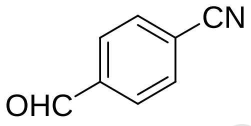
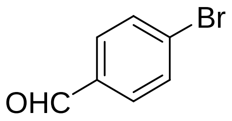
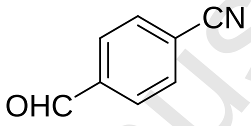
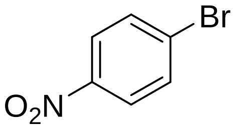
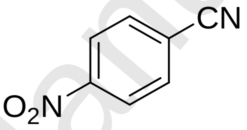
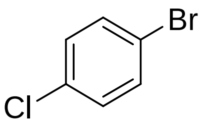
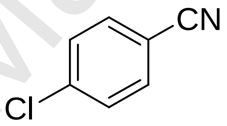
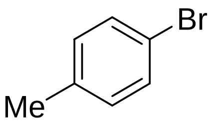
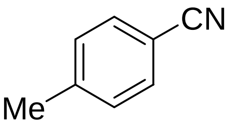
From all above studies and results of Table 2, it is concluded that synergistic effect between copper and palladium nanoparticles, plays an important role in the cyanation of iodobenzene with $K_4[Fe(CN)_6]$. In order to demanstrate the effect of copper species in the $Pd@CuFe_2O_4$ on it's greater reactivity, the model reaction was studied using homogenous Pd and Cu togethre (Table 2, entries 8 and 9) and also in the presance of $Pd@Fe_3O_4$ and $CuCl_2$ additive (Table 2, entry 10). Results showed that presence of copper species have significant effect on palladium catalysts compared to the individual using of Pd or Cu catalysts. These observations clearly support important effect of $CuFe_2O_4$ NPs in high reactivity of $Pd@CuFe_2O_4$ catalyst.

In order to investigate the general application of palladium supported copper ferrite nanaoparticles as a catalyst, reaction of structurally diverse aryl iodides and bromides with $K_4[Fe(CN)_6]$ were studied (Table 3). The results indicated that reaction of aryl iodides proceeded effectively and desired nitrile products were obtained in high to excellent yields. In addition, the reactions of aryl bromides under similar optimized reaction conditions proceeded well and corresponding products were obtained in high yields. The results of Table 3 indicated that presence of electron withdrawing groups at the *para*-position of the aryl halides afforded high yields compared to electron donating groups at the *para*-position. In addition, because of the weakness of the carbon-iodide bond in aryl iodides, these compounds exhibit greater reactivity compared to aryl bromides.

Table 3 Reaction of structurally different aryl iodides and bromides with $K_4Fe(CN)_6$ in the presence of catalyst.



Entry	ArX	Time (h)	Product[a]	Yield%
1		7	 **1a**	97
2		10	 **1b**	95
3		20	 **1c**	93
4		20	 **1d**	95
5		10	 **1e**	94
6		15	 **1f**	89
7		2	 **1g**	98
8		2	 **1h**	98

9		5	 **1i**	97
10		9	 **1j**	92
11		5	 **1k**	95
12		24	 **1k**	71
13		24	 **1g**	78
14		24	 **1h**	75
15		30	 **1b**	73

[a] Reaction conditions: ArX (1 mmol), K_4FeCN_6 (0.6 mmol), K_2CO_3 (1.5 mmol), catalyst (10 mg, containing 0.001 mmol Pd), and DMF (2 mL)

Finally, recycling property of the catalyst was studied for the reaction of iodobenzene with $K_4[Fe(CN)]_6$. After completion of each run, the catalyst was separated by external magnetic rod, washed with diethyl ether and was subjected into another batch of the reaction (Figure 6).

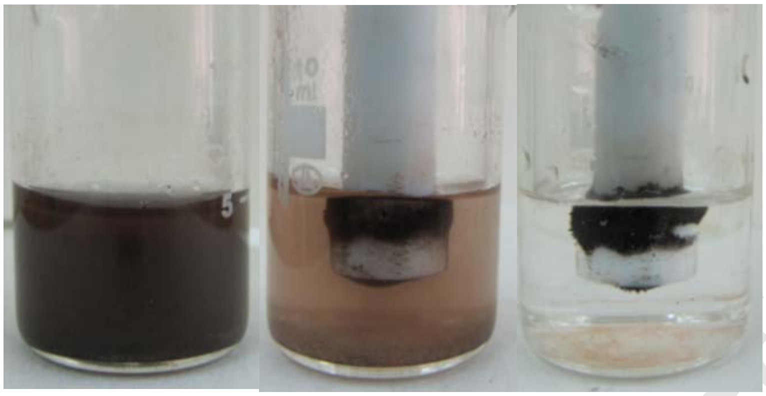


Figure 6. a) reaction mixture, b) isolation of catalyst from reaction by external magnet after 3 min, c) isolation of catalyst from reaction by external magnet after 8 min.

The result showed that catalyst is recoverable and was recycled for four consecutive runs with small drops in catalytic activity (Figure 7).

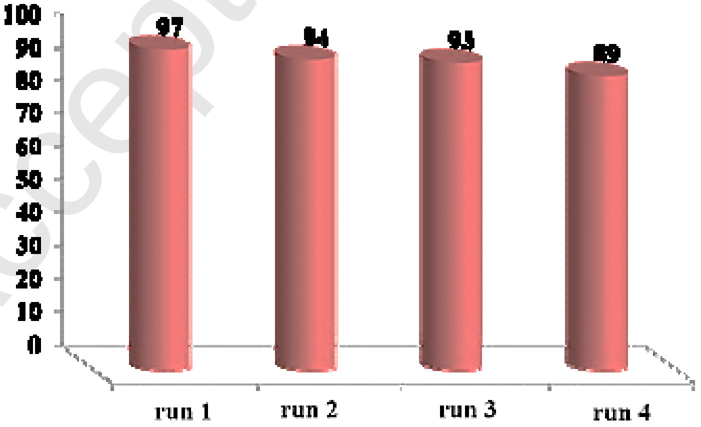
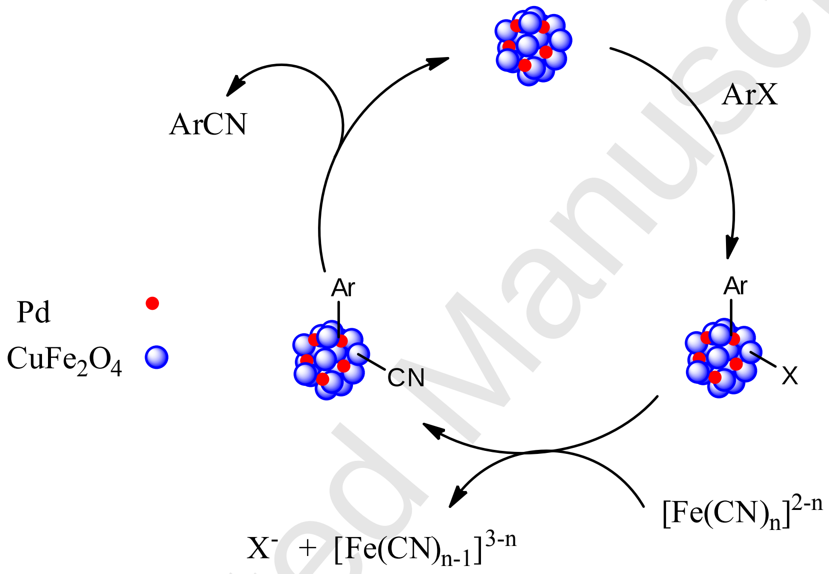


Figure 7. Recycling of catalyst for the reaction of iodobenzene with $K_4Fe(CN)_6$

A possible mechanism for the Pd@$CuFe_2O_4$ catalyzed cyanation reaction involves a well-known mechanism for cyanation of aryl halides which occur on the surface of the catalyst (scheme 3) [40]. Reaction proceeded via the oxidative addition of aryl halide over catalyst followed by cyanide anion transfer from $K_4[Fe(CN)]_6$ and finally reductive elimination step afforded the aryl cyanide product.



Scheme 3. Proposed mechanism for Pd@$CuFe_2O_4$ catalyzed cyanation of aryl halides.

4. Conclusion

In summary, preparation and characteriztion of palladium nanoparticles supported copper ferrite nanoparticles is described. The new heterogeneous catalyst is an efficient and recyclable catalyst in the cyanation of aryl iodides and bromides at low palladium loading condition in comparison to the Fe_3O_4 supported palladium nanoparticles, homogeneous $Pd(OAc)_2$, CuI, $CuCl_2$, Fe_3O_4, and $CuFe_2O_4$ nanoparticles. It may be concluded that the synergitic effect between palladim and copper species is responsible for the observed reactivity. The catalyst showed good recyclability using external magnet and was reused for four times with small drops in catalytic activity.

Acknowledgment

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 93020713) for support of this work.

References

[1] A. Kleemann, J. Engel, B. Kutscher, D. Reichert, Pharmaceutical substances: syntheses, patents, applications, 4th ed., Georg Thieme, Stuttgart, 2001.

[2] Larock, R. C. Comprehensive Organic Transformations; VCH: New York, 1989.

[3] Z. Rappoport, Chemistry of the Cyano Group; John Wiley & Sons: London, U.K, 1970; b) R. C. Larock, In Comprehensive Organic Transformations: A Guide to Functional Group Preparations; VCH: New York, U.S.A, 1989.

[4] J. Lindley, Tetrahedron 40 (1984) 1433-1456.

[5] K. W. Rosenmund, E. Struck, Ber. Dtsch. Chem. Ges. 2 (1919) 1749-1755.

[6] V. Braun, J. Justus, Liebigs Ann. Chem. 488 (1931) 111-126.

[7] D. T. Mowry, Chem. Rev. 42 (1948) 189-283.

[8] G. P. Ellis, T. M. Romney-Alexander, Chem. Rev. 87 (1987) 779-794.

[9] T. Sandmeyer, Ber. Dtsch. Chem. Ges. 17 (1884) 1633-1635.

[10] C. Galli, Chem. Rev. 88 (1988) 765-792.

[11] P. Anbarasan, T. Schareina, M. Beller, Chem. Soc. Rev. 40 (2011) 5049-5067.

[12] H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, Chem. Eur. J. 11 (2005) 2483–2492.

[13] Y. Ren, Z. Liu, S. Zhao, X. Tian, J. Wang, W. Yin, S. He, Catal. Commun. 10 (2009) 768-771.

[14] T. Schareina, A. Zapf, W. Mägerlein, N. Müller, M. Beller, Chem. Eur. J. 13 (2007) 6249-6254.

[15] H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, Chem. Eur. J. 11 (2005) 2483-2492.

[16] J. Zanon,; A. Klapars, S. L. Buchwald, J. Am. Chem. Soc. 125 (2003) 2890-2891.

[17] Q. Wen, J. Jin, Y. Mei, P. Lu, Y. Wang, Eur. J. Org. Chem. (2013) 4032-4036.

[18] C. DeBlase, N. E. Leadbeater, Tetrahedron 66 (2010) 1098-1101.

[19] Z. Jiang, Q. Huang, S. Chen, L. Long, X. Zhou, Adv. Synth. Catal. 354 (2012) 589-592.

[20] A. B. Pawar, S. Chang, Chem. Commun. 50 (2014) 448-450.

[21] R. K. Arvela, N. E.Leadbeater, J. Org. Chem. 68 (2003) 9122-9125.

[22] P. Anbarasan, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 50 (2011) 519-522.

[23] B. A. Anderson, E. C. Bell, F. O. Ginah, N. K. Harn, L. M. Pagh, J. P. Wepsiec, J. Org. Chem. 63 (1998) 8224-8228.

[24] C.Yang, J. M.Williams, Org. Lett. 6 (2004) 2837-2840.

[25] H.-J. Cristau, A. Ouali, J.-F. Spindler, M. Taillefer, Chem. Eur. J. 11 (2005) 2483-2492.

[26] M. Sundermeier, A. Zapf, S. Mutyala, W. Baumann, J. Sans, S. Weiss, M. Beller, Chem. Eur. J. 9 (2003)1828-1836.

[27] H.-Q. Do, O. Daugulis, Org. Lett. 12 (2010) 2517-2519.

[28] T. Okano, M. Iwahara, J. Kiji, Synlett (1998) 243-244.

[29] J. Zanon, A. Klapars, S. L. Buchwald, J. Am. Chem. Soc. 125 (2003) 2890-2891.

[30] B. Wang, R. Zhao, B.-C. Chen, B. Balasubramanian, Arkivoc (2010) 47-52.

[31] H. Yu, R. N. Richey, W. D. Miller, J. Xu, S. A. May, J. Org. Chem. 76 (2011) 665-668.

[32] M. Alterman, A. Hallberg, J. Org. Chem. 65 (2000) 7984-7989.

[33] R. Chidambaram, Tetrahedron Lett. 45 (2004) 1441-1444.

[34] R. S. Jensen, A. S. Gajare, K. Toyota, M. Yoshifuji, F. Ozawa, Tetrahedron Lett. 46 (2005) 8645-8647.

[35] F. G. Buono, R. Chidambaram, R. H. Mueller, R. E.Waltermire, Org. Lett. 10 (2008) 5325-5328.

[36] A. Zhang, J. L. Neumeyer, Org. Lett. 5 (2003) 201-203.

[37] N. Chatani, T. Hanafusa, J. Org. Chem. 51 (1986) 4714-4716.

[38] M. Sundermeier, S. Mutyala, A. Zapf, A. Spannenberg, M. Beller, J. Organomet. Chem. 684 (2003) 50-55.

[39] T. Schareina, A. Zapf, M. Beller, Chem. Commun. (2004) 1388-1389.

[40] T. Schareina, A. Zapf, M. Beller, J. Organomet. Chem. 689 (2004) 4576-4583.

[41] S. A. Weissman, D. Zewge, C. Chen, J. Org. Chem. 70 (2005) 1508-1510.

[42] G. Chen, J. Weng, Z. Zheng, X. Zhu, Y. Cai, J. Cai, Y. Wan, Eur. J. Org. Chem. (2008) 3524-3528.

[43] P. Y. Yeung, C. M. So, C. P. Lau, F. Y. Kwong, Org. Lett. 13 (2011) 648-651.

[44] J. Kim, H. J. Kim, S. Chang, Angew. Chem. Int. Ed.51 (2012) 11948–11959.

[45] J. Shi, Chem. Rev. 113 (2013) 2139–2181

[46] R. Chinchilla, C. Nájera, Chem. Soc. Rev. 40 (2011) 5084-5121.

[47] S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. V. Elst, R. N. Muller, Chem. Rev. 108 (2008) 2064-2110.

[48] M. L. Kantam, J. Yadav, S. Laha, S. Jha, Synlett (2009) 1791-1794.

[49] Y. L. N. Murthy, B. S. Diwakar, B. Govindh, K. Naglakashmi, I. V. K. Viswanath, R. Singh, J. Chem. Sci. 124 (2012) 639-645.

[50] R. Zhang, J. Liu, S. Wang, J. Niu, C. Xi, W. Sun, ChemCatChem 3 (2011) 146-149.

[51] V. Avudoddi, V. K. G. Palle, V. R. Pallapothula, Eur. J. Chem. 3 (2012) 298-304.

[52] S. Yang, C. Wu, H. Zhou, Y. Yang, Y. Zhao, C. Wang, W. Yang, J. Xua, Adv. Synth. Catal. 355 (2013) 53-58.

[53] S. Yang, W. Xie, H. Zhou, C. Wu, Y. Yang, J. Niu, W. Yang, J. Xu, Tetrahedron 69 (2013) 3415-3418.

[54] K. Swapna, S. N. Murthy, M. T. Jyothi, Y. V. D. Nageswar, Org. Biomol. Chem. 9 (2011) 5989-5996.

[55] N. Panda, A. K. Jena, S. Mohapatra, Appl. Catal. A 433-434 (2012) 258-264.

[56] R. Zhang, C. Miao, Z. Shen, S. Wang, C. Xia, W. Sun, ChemCatChem. 4 (2012) 824-830.

[57] K. Swapna, S. N. Murthy, Y. V. D. Nageswar, Eur. J. Org. Chem. (2011) 1940-1946.

[58] K. H. V. Reddy, G. Satish, K. Ramesh, K. Karnakar, Y. V. D. Nageswar, Chem. Lett. 41 (2012) 585-587.

[59] D. Kundu, N. Mukherjee, B. C. Ranu, RSC Adv. 3 (2013) 117-125.

[60] N. Panda, A. K. Jena, S. Mohapatra, S. R. Rout, Tetrahedron Letters 52 (2011) 1924–1927.

[61] M. Gholinejad, B. Karimi, F.Mansouri, J. Mol. Cat. A. Chem. 386 (2014) 20-27.

[62] M. Shen, H. Cai, X. Wang, X. Cao, K. Li, S. H. Wang, R. Guo, L. Zheng, G. Zhang, X. Shi, Nanotechnology 23(2012) 10560-105070

[63] A. L. Andrade, D. M. Souza, M. C. Pereira, J. D. Fabris, R. Z. Domingues, Cerâmica 55 (2009) 420-424.

[64] M. Dai, J. Kwon, Y. J. Chabal, M. D. Halls, R. G. Gordon, Mater. Res. Soc. Symp. Proc. 1155 (2009) C11-06.

[65] H. Firouzabadi, N. Iranpoor, M. Gholinejad, Tetrahedron 65 (2010) 7079-7084.

Research highlights

- Pd@$CuFe_2O_4$ NPs were synthesized and characterized for the first time.
- The low loading Pd catalyst shows good activity in the cyanation of aryl iodides and bromides.
- Synergitic effect between Pd and Cu species is responsible for the observed reactivity.
- The Magnetically recoverable catalyst was recycled for four times with small drops in activity.

Palladium Nanoparticles Supported on Magnetic Copper Ferrite Nanoparticles: The Synergistic Effect of Palladium and Copper for Cyanation of Aryl Halides with $K_4[Fe(CN)_6]$

Mohammad Gholinejad [a*] Afsaneh Aminianfar [a]

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gava zang, Zanjan 45137-6731, Iran.

Email: gholinejad@iasbs.ac.ir

[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences, Gava Zang, Zanjan 45137-66731, Iran; email: gholinejad@iasbs.ac.ir

Pd supported on $CuFe_2O_4$ NPs were synthesized, characterized and successfully applied as magnetically recyclable catalyst for the cyanation of aryl iodides and bromides.