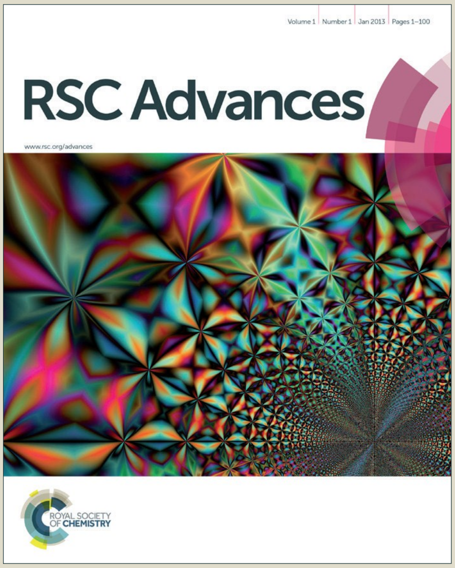
RSC Advances



Journal Name

ARTICLE

Copper acetate/2-aminobenzenthiol complex supported on magnetite/silica nanoparticles as a highly active and recyclable catalyst for 1,2,3-triazoles Synthesis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abbas Ali Jafari,[a,b*] Hajar Mahmoudi[a,b] and Habib Firouzabadi[c*]

A novel and recoverable Cu(II)/ 2-aminobenzenthiol complex immobilized on magnetite/silica nanoparticles (Fe_3O_4/SiO_2 NPs) catalyzed synthesis of 1,2,3-triazole derivatives via a three-component condensation of terminal alkynes, benzyl or alkyl halides, and sodium azide in wet polyethylene glycol (PEG 400/H_2O) as a *green* media at ambient temperature. The catalytic potentials of some transition metal salt complexes adhered on Fe_3O_4/SiO_2 NPs (5-10 nm) were employed for the one pot 1,2,3-triazole synthesis. The order of catalytic activity of various transition metal salt complexes for a model reaction was found to be Cu(II) > AgI ~ CuI > CuCl > $Ni(OAc)_2$ ~ $Co(OAc)_2$ > $ZnCl_2$. Moreover, the order of catalytic activity of Cu(II) salts supported on Fe_3O_4/SiO_2 NPs was found to be $Cu(OAc)_2$ > $CuSO_4$ ≫ $CuCl_2$ > $Cu(NO_3)_2$. The catalytic potential of the complex has been improved significantly when the core-shell magnetite/silica has been used instead of magnetite for successful wide-spread syntheses of 1-aryl-1,2,3-triazoles under mild reaction conditions. 1-aryl-1,2,3-triazoles syntheses require harsh reaction conditions.

Introduction

The 1,2,3-triazole moiety, a key structural element of many natural products, pharmaceuticals and synthetic agents, has increasingly attracted the synthetic pursuit of chemists because of its important biological properties.[1-4] So far, numerous synthetic methods have been developed and reported in litrature.[5-9] One of the most popular protocol for the preparation of these compounds is 1,3-dipolar "Huisgen" cycloaddition reaction which is catalyzed by Cu(I) and ruthenium(II).[10, 11] By this reaction, 1,4- or 1,5-disubstituted 1,2,3-triazoles are prepared with high regiospecificity. But the inherent thermodynamic instability of Cu(I) enforces conditions like inert atmosphere, anhydrous solvents along with the formation of undesired by-products.[12, 13] Development of new methods and catalysts for the synthesis of the aforementioned target molecules under cleaner and milder reaction conditions is of demands. Along this interest, protocols such as; the *in situ* generation of Cu(I) catalyst by the reduction of Cu(II) or oxidation of Cu(0) to Cu(I) or using stable Cu(II) complexes of oligopyridines with electron-donating groups have been developed.[14-17] Meanwhile, a few strategies using heterogeneous copper catalysts are available in which the copper moiety is immobilized on zeolite, activated carbon and polymer compounds. By this mean, the catalytic activity of the catalysts has been improved and their recovery has been more facilitated.[5, 8, 15-20] But in practice, separation of the catalysts from the reaction mixture still encounter difficulties and is a time- and an energy-consuming process.

Recently, some attempts have started to prepare catalysts supported on magnetic nanoparticles (MNPs) which are easily separable by an external magnetic field from the reaction mixtures. This is highly beneficial for large-scale operation in pharmaceutical and food industries and minimizes the contamination of the final products with the metal catalysts. In this respect, we have recently reported new magnetic catalysts and reagents used in basic organic reactions.[21-26]

However, it should be declared that, the naked MNPs are extremely chemically active and are easily oxidized in the air.[27] Therefore, their protection and the coating of the naked MNPs with organic or inorganic layers is a valuable strategy which also provides useful sites for further functionalization of the material.[28,29]

Considering the less costs with much higher purity of Cu(II) salts in comparison with the corresponding Cu(I) salts, herein we report preparation of a novel and amagnetically recoverable $Cu(OAc)_2$/2-aminobenzenthiol complex immobilized on magnetite/silica nanoparticles (Fe_3O_4/SiO_2NPs). This magnetic composite has been successsfully used as a catalyst for the synthesis of 1,2,3-triazole derivatives *via* a three-component condensation of terminal alkynes, benzyl or alkyl halides, in the presence of sodium azide under mild conditions.

---

[a] *Chemistry Department, College of science, Yazd University, 89195-741 Yazd, Iran. E-mail: jafari@yazd.ac.ir*
[b] *Innovation Center, Yazd Science and Technology Park, Yazd, Iran.*
[c] *Late Professor Moshfegh Laboratory, Chemistry Department, Shiraz University, Shiraz 71454, Iran. E-mail: firouzabadi@chem.susc.ac.ir*

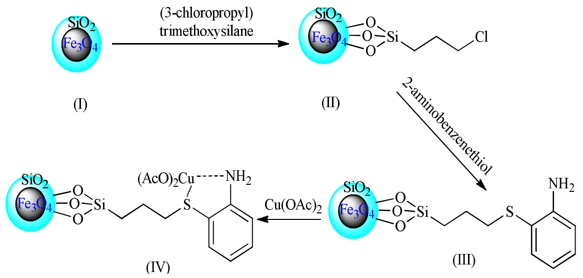
† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Results and discussion

Magnetite/silica nanoparticles (Fe_3O_4/SiO_2NPs) of 5-10 nm size were prepared according to the reported reverse micelle procedure as presented in supporting information (S1).[30] By this method, a micro emulsion was prepared by dissolving sodium dodecylbenzenesulfonate in xylene by sonication. Then a solution composed of $FeCl_2.4H_2O$, $Fe(NO_3)_3.9H_2O$ was added to the micro emulsion under vigorous stirring with heating under argon atmosphere. Hydrazine was injected into the reverse-micelle solution. The resulting mixture was heated at 90˚C and then was cooled down to 40˚C in an appropriate time. To the resulting mixture, tetraethoxy silane (TEOS) was added with stirring. The resulting solid material was washed with sodium phosphate buffer solution (pH 7.4) to give $Fe_3O_4@SiO_2$ NPs which were dried at room temperature under vacuum and characterized by XRD, FTIR.[30]

The preparation steps of the $Cu(OAc)_2$/2-aminobenzenethiol complex immobilized on magnetite/silica nanoparticles ($Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$) are shown in Scheme 1.



Scheme 1.

The progress of the reaction steps, as demonstrated in Scheme 1, are in accord with their FT-IR spectra as presented in Fig. 1.

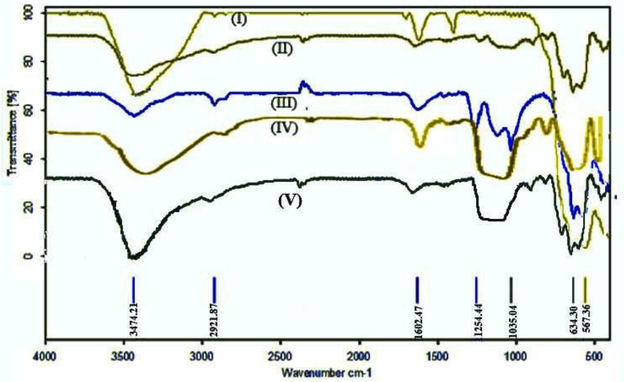


Figure 1. FT-IR spectra of $Fe_3O_4@SiO_2$ (I), $Fe_3O_4@SiO_2$/(3-chloropropyl) trimethoxysilane (II), $Fe_3O_4@SiO_2$/ABT (III), $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ (IV) and $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ after the 1st run of recycling for the synthesis of 1-benzyl-1,2,3-triazole as a model reaction (V) which is similar to (IV).

The vibration bands at 557 and 1035 cm^{-1} are the typical IR absorbance induced by Fe-O vibration and stretching vibrations of the Si–O respectively (Fig. 1 (I)). By supporting (3-chloropropyl) trimethoxysilane moiety on $Fe_3O_4@SiO_2$, the intensity of O-H band at 3000-3600 cm^{-1} has been decreased. The vibration band of CH_2 aliphatic at 2921 cm^{-1} shows that the (3-chloropropyl) trimethoxysilane moiety has been functionalized on the surface of the $Fe_3O_4@SiO_2$ (Fig. 1 (II)). The increased intensity of the bands at 1035, 1100, 1254, and the broadening of the peak at 1632 cm^{-1} is due to nucleophilic substitution of Cl with S atom of 2-aminobenzthiol. The band in 3000-3600 cm^{-1} region has become sharper which is due to the presence of NH_2 functional group (Fig. 1,III). By the copper acetate complex formation with $Fe_3O_4@SiO_2$/ABT, the band intensity at 1632 cm^{-1} has been increased and the band in the region of 3000-3600 cm^{-1} has become broader (Fig. 1, IV). The resulting new magnetic composite has been further characterized by XRD, XRF, TEM and VSM techniques. The amount of copper(II)acetate supported on Fe_3O_4/SiO_2NPs was determined by atomic absorption method to be in the range of 2.8-3.0 ($mmolg^{-1}$) (Fig S1, Supporting Information). X-ray diffraction analysis confirms the structural order of the $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ compounds and approves the existence of copper acetate on $Fe_3O_4@SiO_2$ material (Fig S2). X-ray fluorescence analysis of $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ also (Table S3) demonstrates the presence of $Cu(OAc)_2$ moiety in the material attached to the magnetite surface.

The magnetization curves of the Fe_3O_4 ,$Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ nanoparticles recorded at room temperature exhibit a super paramagnetic behavior (zero coercivity and remanence on the magnetization loop) (Fig. 2). The saturation magnetization value of the $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ is 17 $emug^{-1}$ (Fig. 2c). This number is three times lower than that of naked $Fe_3O_4@SiO_2$ (Fig. 2b, 55 $emug^{-1}$). This is due to the shielding of the $Fe_3O_4@SiO_2$ surface with the coating material.

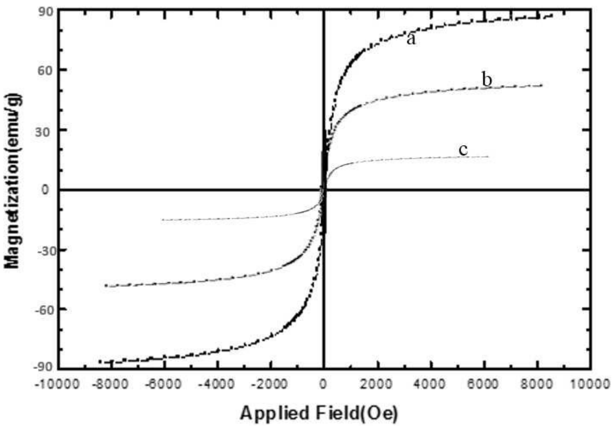


Figure 2. Comparison of magnetization loops of a) Fe_3O_4 with b) $Fe_3O_4@SiO_2$[30] and with c) $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ composite.

The thermogravimetric analysis of $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ as shown in Fig. S6, indicates the weight loss (2.27%) in the temperature range of 120-180˚C. This weight loss is mainly related to dehydration of the composite. When the temperature is raised to the range of 240-280˚C, another weight loss (3.21%) is observed, which is attributed to the decomposition of AcO. The third mass loss (22.15%) is observed when the temperature reaches to the range of 300–600˚C. This corresponds to the thermal decomposition of ABT.

Transmission electron microscopy (TEM) image of $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ shows the spherical morphology of the material with an average size of 5-10 nm (Fig.3,a). The TEM image of the composite used as a catalyst for the synthesis of 1-benzyl 1,2,3-triazole as a model reaction after the 1st run of its recycling 9Fig.3,b) showed conservation of its morphology and the size of the particles size (5-10 nm) (Fig 3).

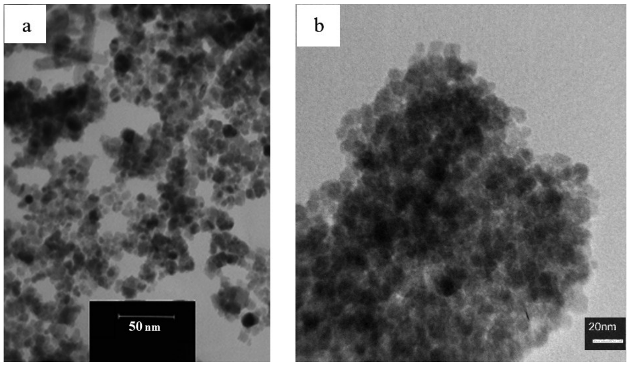
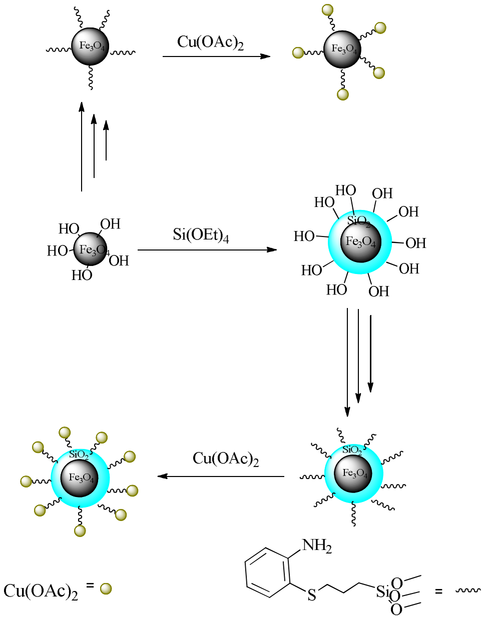


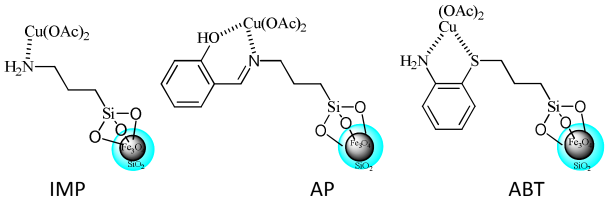
Figure 3. TEM images of $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ before (a) and after the 1st run of recycling (b)for the synthesis 1-benzyl-1,2,3-triazole



Scheme 2

When the core-shell magnetite/silica was employed as a support instead of magnetite, the amount of the supported copper and also the catalytic activity of the complex was significantly improved. A good connectivity of silan group of ABT ligand with SiO_2 improves the number of sites for the complex formation with $Cu(OAc)_2$ and as a result, improving the amounts of the copper moiety supported on the shell-core and improving the catalytic activity of the composite (Scheme 2). We have also performed the control experiment with copper salt complex with ABT is immobilized on silica particles for the model reaction. The results obtained for the catalytic activity of silica catalyst was similar with the magnetic one.

The stability of the complexes of $Cu(OAc)_2$ with electron-donating ligands such as 3-amino propyl (AP), 2-iminomethylphenol (IMP) and 2-aminobenzenethiol (ABT) (Scheme 3), attached to the core of magnetite/silica nanoparticles were examined by measuring the amounts of leaching of Cu(II) into the reaction mixtures.



Scheme 3

This was studied by graphite furnace atomic absorption analysis and hot filtration test. The ABT ligand (Scheme 3) showed the least amount of leaching in comparison with the other two ligands; IMP and AP in this study (Table S4). The hot filtration test was also studied for $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ catalyst in the reaction of 1,2,3-triazol synthesis. The reaction was not proceeded after separating the catalyst by a permanent magnet. It was compulsory to analyze the filtered reaction mixture by atomic absorption analysis to confirm the absence of metal.

The recycling ability of the complexes with various ligands (Scheme 3, IMP, AP, ABT) was investigated for the synthesis of 1-benzyl-1,2,3-triazole starting from benzyl bromide, phenyl acetylene and sodium azide as a model reaction (Fig. 4). The recycling of the catalysts was repeated for 5 consecutive runs for the reaction. In this regard, ABT ligand proved to be the best reusable catalyst in this respect.

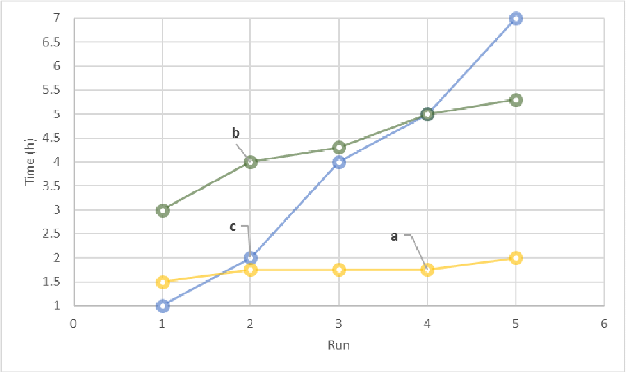
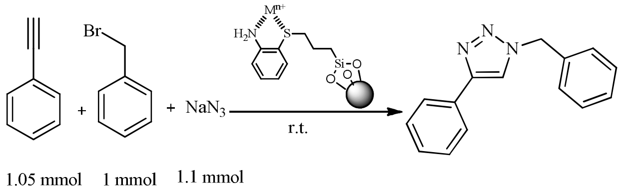


Figure 4. The recycling of the catalysts a) $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$, b) $Fe_3O_4@SiO_2$/IMP-$Cu(OAc)_2$ and c) $Fe_3O_4@SiO_2$/AP-$Cu(OAc)_2$ for the synthesis of 1-benzyl-1,2,3-triazole as a model reaction.

The catalytic activity of various metal salts such as $Cu(NO_3)_2$, $Cu(SO_4)_2$, $CuCl_2$, AgI, CuI, CuCl, $Ni(OAc)_2$, $Co(OAc)_2$, $ZnCl_2$ complexed with $Fe_3O_4@SiO_2$/ABT for the synthesis of 1-benzyl-1,2,3-triazole as a model reaction at ambient temperature in different media was also investigated (Table 1) (Fig. S5). The best result was obtained when $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ was used in PEG/water (9:1) as a the solvent (Table 1, Entry 18).

Table 1. The optimization results obtained for the reaction of benzyl bromide with phenyl acetylene and sodium azide.

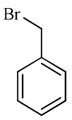
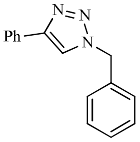
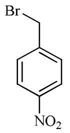
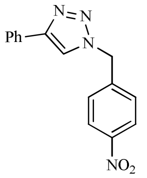
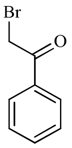
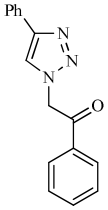
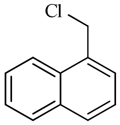
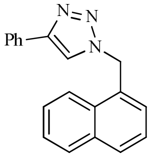
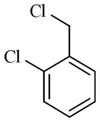
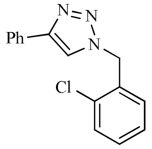
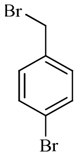
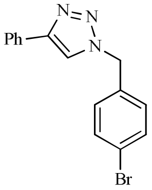
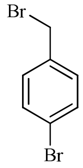
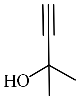
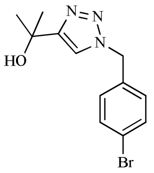
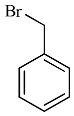
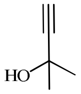
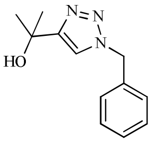


Entry	M^{a}	Solvent^{b}	Time (h)	Yield (%)
1	-	-	8	20
2	CuI^{c,d}	-	1.5	80
3	CuCl^{c,d}	-	2	85
4	AgI^{c,d}	-	1.15	80
5	$Ni(OAc)_2$	-	8	50
6	$Co(OAc)_2$	-	8	50
7	$ZnCl_2$	-	8	50
8	$Cu(NO_3)_2$	-	3	91
9	$CuSO_4$	-	1.5	92
10	$CuCl_2$	-	2	93
11	$Cu(OAc)_2$	-	1	92
12	$Cu(OAc)_2$	H_2O	8	30
13	$Cu(OAc)_2$	EtOH	8	10
14	$Cu(OAc)_2$	PEG	8	30
15	$Cu(OAc)_2$	PEG/H_2O(1:1)	5	96
16	$Cu(OAc)_2$	PEG/H_2O(2:1)	3	94
17	$Cu(OAc)_2$	PEG/H_2O(4:1)	1	95
18	**$Cu(OAc)_2$**	**PEG/H_2O(9:1)**	**0.25**	**95**
19	$Cu(OAc)_2^{e}$	PEG/H_2O(9:1)	0.5	97
20	$Cu(OAc)_2^{f}$	PEG/H_2O(9:1)	0.2	92
21	$Cu(OAc)_2^{g}$	PEG/H_2O(9:1)	0.08	93
22	$Cu(OAc)_2^{h}$	PEG/H_2O(9:1)	0.05	92
23	$Cu(OAc)_2$	EtOAc	8	10
24	$Cu(OAc)_2$	CH_3CN	8	10
25	$Cu(OAc)_2$	n-Hexane	8	5

^{a}Catalyst (2 mol%), ^{b}solvent (1 mL), ^{c}under N_2 atmosphere, ^{d}by-product observed, ^{e}catalyst (1 mol%), ^{f}catalyst (4 mol%), ^{g}at 50 °C, ^{h}at 100 °C

Then, the obtained optimized conditions were applied for the reaction of different alkynes with various benzyl halides and sodium azide as summarized in Table 2.

Table 2. 1-benzyl-1,2,3-triazoles synthesis using benzyl bromides, terminal acetylenes and sodium azide

Entry	Benzyl halide	Acetylene	Product	Time (min)	Yield (%)
1				15	95
2				60	90
3				120	85
4				60	92
5				100	90
6				10	90
7				10	95
8				10	90

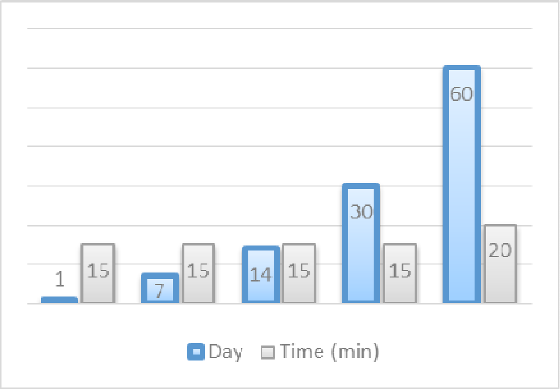


Figure 5. The life span of $Fe_3O_4@SiO_2$/ABT-$Cu(OAc)_2$ showing the stability of the catalyst

We have also extended the scope of the use of the catalyst to the reaction of varieties of diazonium salts with various terminal acetylenes and sodium azide under optimized conditions (Table S7). As shown in Table 3, diazonium salts bearing either electron-withdrawing or electron-donating substituents on the benzene ring afforded the corresponding 1-aryl-1,2,3-triazole products in excellent yields (Table 3, Entries 1,2,6,7).

Table 3. 1-Aryl-1,2,3-triazole synthesis using diazonium salts, terminal acetylenes and sodium azide

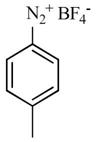
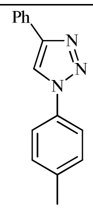
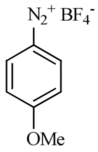
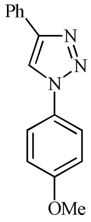
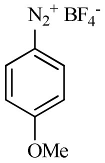
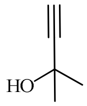
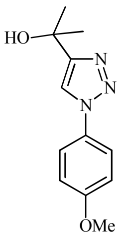
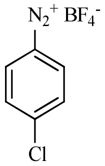
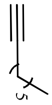
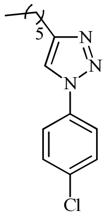
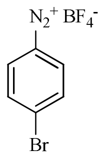
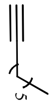
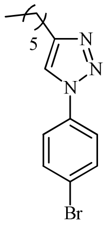
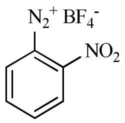
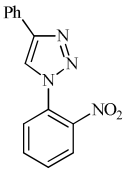
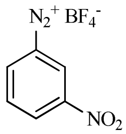
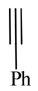
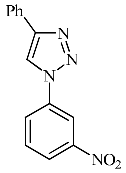
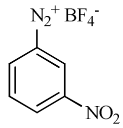
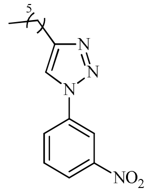
Entry	Diazonium salt	Acetylene	Product	Time (min)	Yield (%)
1				60	95
2				60	85
3				45	90
4				35	95
5				50	92
6				240	90
7				300	90
8				120	92

Table 4. Comparison of the catalytic activity of different catalysts and conditions for the synthesis of 1-benzyl-1,2,3-triazole

Entry	Catalyst	Solvent ^{b}	Temp. (˚C)	Time (h)	Yield (%)
1	Cu/Charcoal[5]	H_2O	100	0.6	91
2	CuO[31]	THF/H_2O (0.4 M)	60	24	95
3	tris(triazolyl)methanol–Cu(I)[32*]	MeOH:H2O (1 : 1)	40	4	99
4	$Cu_3N/Fe_3N@SiO_2$[33]	Et_3N/CH_3CN	25	3	84
5	Cu-Apatite[34]	H_2O	100	1.5	99
6	Cu NPs/Carbon[35]	THF/NEt_3	65	0.16	98
7	Amberlyst A-21-CuI[36*]	CH_2Cl_2	25	18	97
8	SiO_2–NHC–Cu(I)[37*]	-	25	0.5	93
9	**$Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$**	**PEG/H_2O(9:1)**	**25**	**0.25**	**95**

*under N_2 atmosphere

The catalytic activity of $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$ in comparison with some other reported catalysts for the synthesis of 1-benzyl-1,2,3-triazole is presented. In the presence of this catalyst, the reaction proceeded at ambient temperature within 0.25 h in 95% yield of the desired product (Table 4, Entry 9). Comparison of the results in Table 4, shows an obvious advancement of using $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$ catalyst with respect to its easy separation by an external magnetic field without using filtration, centrifugation or sedimentation techniques, which are all energy and time-consuming processes. The catalyst recycling with good recycling cycles along with a negligible amount of leaching of the metal with a long life span of the catalyst, are the advancements observed by using this catalyst for the reaction. The media in which the catalyst is highly active is wet PEG that is an eco-friendly media. In addition, in the presence of this catalyst the target molecules are produced with excellent yields.

Experimental

Materials and methods

All commercially available chemicals were obtained from Merck and Fluka Chemical Companies, and used without further purification unless otherwise stated; Solvents were distilled before their use. The products were characterized by FTIR, ^{1}HNMR (500 MHz) and ^{13}CNMR (125 MHz) spectroscopy.

All the reactions were monitored by thin layer chromatography (TLC) coated with silica gel illuminated with UV light and iodine as the reagent. All yields refer to the isolated products.

Synthetic procedures

Preparation of $Fe_3O_4@SiO_2$-(3-chloropropyl)trimethoxysilane: silica-coated Fe_3O_4NPs that was prepared by reverse micelle method[30] (1 g) was added to toluene (5 mL) and under nitrogen atmosphere. Then, (3-chloropropyl)trimethoxysilane (0.4 mL) was added and the mixture was slowly heated to 90 °C and was kept at this temperature for 6h. The brown precipitates were collected with an external magnet and washed with aqueous buffer (100 mm sodium phosphate, pH 7.4). The resulting precipitates were dried for 12 h at room temperature under vacuum and characterized by FTIR (Scheme1).

Preparation of $Fe_3O_4@SiO_2$-ABT: $Fe_3O_4@SiO_2$-(3-chloropropyl) trimethoxysilane (1 g) as prepared in the above section, was added to ethanol (5 mL) and dispersed under ultrasound irradiation for 15 min. Then, 2-aminobenzenethiol (1.1 mL) was slowly added to the mixture under vigorous stirring for 6h. The brown precipitates were collected with an external magnet and washed with ethanol (10 mL). The resulting precipitates were dried for 12h at room temperature under vacuum and characterized by FTIR (Scheme 1).

Preparation of the $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$: $Fe_3O_4@SiO_2$-ABT as prepared (1 g) in the preceding section, was added to ethanol (5 mL) and dispersed under ultrasound irradiation for 15 min. Then copper acetate (0.6 g) was added to the mixture under vigorous stirring for 6h. The light brown precipitates were collected with an external magnet and washed with ethanol (10 mL). The resulting precipitates were dried for 12h at room temperature under vacuum and characterized by FTIR, XRD, XRF, VSM, TEM (Scheme1).

Synthesis of 1-benzyl-1,2,3-triazole, **a model reaction:** $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$ (0.02 mmol, 0.04 g) was added to a stirring mixture of acetylene (1.05 mmol), benzyl halides (1 mmol) and sodium azide (1.1 mmol, 0.07 g) in H_2O/PEG 600 (1:9, 1 mL) mixture at room temperature. The progress of the reaction was monitored by TLC (hexane/ethylacetate eluent 4:1). After completion of the reaction, the desired 1-benzyl-1,2,3-triazole product was separated by extraction with diethyl ether from the reaction mixture. The product was obtained after concentration of the diethyl ether as highly pure crystalline compounds in good to excellent yields (Table 2).

General procedure for the synthesis of 1-aryl 1,2,3-triazoles: $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$ (0.02 mmol, 0.04 g) was added to a stirring mixture of acetylene (1.05 mmol), diazonium salt (1 mmol) and sodium azide (1.1 mmol, 0.07 g) at 70 °C in H_2O (1 mL). The progress of the reaction was monitored by TLC (hexane/ethylacetate eluent 3:2). After completion of the reaction, ethanol (2 mL) was added to the reaction mixture. The catalyst was separated by a permanent magnet from the reaction mixture. The desired 1-aryl-1,2,3-triazole product were obtained after concentration of the reaction mixture under diminished pressure as highly pure powder compounds in good to excellent yields (Table 3).

Conclusions

In conclusion, in this study, a facile preparation of a new magnetic composite in which Fe_3O_4Nps are walled with SiO_2 particles which carrying many branches composed of a siloxypropyl aminobenzenethiol moiety. This solid magnetic composite has a high capacity for the preparation of many different transition metal complexes. In this paper, we have reported the preparation of Cu(OAc)$_2$ complex which has been applied as a high capacity catalyst with a long endurance catalytic activity for the preparation of 1,2,3-triazole compounds with excellent yields.

The results of this study show advances for the use of $Fe_3O_4@SiO_2$-ABT/Cu(OAc)$_2$ with respect to the other catalysts used for the similar reactions discussed in this article. The catalyst can be easily separated from the reaction mixture by an external magnetic field. This property saves time and energy with respect to filtration or decantation techniques.The reactions proceeded at room temperature in wet PEG400 as an entirely green and safe media in a short reaction time. All the reactions proceeded well with excellent isolated yields.

Acknowledgements

The authors are appreciative to the Research Council of Yazd University for financial support. H. Mahmoudi is grateful to Dr. Mohammad Javad Faghihi for his generous supports during this work and H.F. is appreciative for the grant (BN048) from National Elite Foundation of Iran.

Notes and references

1. V. D. Bock, D. Speijer, H. Hiemstra and J. H. van Maarseveen, *Org. Biomol. Chem.*, 2007, **5**, 971-975.
2. D. R. Buckle, C. J. M. Rockell, H. Smith and B. A. Spicer, *J. Med. Chem.*, 1986, **29**, 2262-2267.
3. A. C. Cunha, J. M. Figueiredo, J. L. M. Tributino, A. L. P. Miranda, H. C. Castro, R. B. Zingali, C. A. M. Fraga, M. C. l. B. V. de Souza, V. F. Ferreira and E. J. Barreiro, *Biorg. Med. Chem.*, 2003, **11**, 2051-2059.
4. A. Brik, J. Alexandratos, Y.-C. Lin, J. H. Elder, A. J. Olson, A. Wlodawer, D. S. Goodsell and C.-H. Wong, *ChemBioChem*, 2005, **6**, 1167-1169.
5. H. Sharghi, R. Khalifeh and M. M. Doroodmand, *Adv. Synth. Catal.*, 2009, **351**, 207-218.
6. X. Xiong, L. Cai, Y. Jiang and Q. Han, *ACS Sustain. Chem. Eng.*, 2014, **2**, 765-771.
7. E. Tasca, G. La Sorella, L. Sperni, G. Strukul and A. Scarso, *Green Chem.*, 2015, **17**, 1414-1422.
8. N. Mukherjee, S. Ahammed, S. Bhadra and B. C. Ranu, *Green Chem.*, 2013, **15**, 389-397.
9. B. S. P. Anil Kumar, K. Harsha Vardhan Reddy, B. Madhav, K. Ramesh and Y. V. D. Nageswar, *Tetrahedron Lett.*, 2012, **53**, 4595-4599.

10. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem.*, 2002, **114**, 2708-2711.
11. J. S. Oakdale and V. V. Fokin, in *Organic Syntheses*, John Wiley & Sons, Inc., 2003, DOI: 10.1002/0471264229.os090.09.
12. F. Alonso and M. Yus, *ACS Catal.*, 2012, **2**, 1441-1451.
13. J. K. Burdett and S. Sevov, *J. Am. Chem. Soc.*, 1995, **117**, 12788-12792.
14. H. Sharghi, S. Ebrahimpourmoghaddam, M. M. Doroodmand and A. Purkhosrow, *Asian J. Org. Chem.*, 2012, **1**, 377-388.
15. X. Xu and D. W. Goodman, *J. Phys. Chem.*, 1993, **97**, 683-689.
16. F. Boccuzzi and A. Chiorino, *J. Phys. Chem.*, 1996, **100**, 3617-3624.
17. A. Wöllner, F. Lange, H. Schmelz and H. Knözinger, *Appl. Catal., A*, 1993, **94**, 181-203.
18. H. Yahiro, K. Nakaya, T. Yamamoto, K. Saiki and H. Yamaura, *Catal. Commun.*, 2006, **7**, 228-231.
19. T. R. Chan and V. V. Fokin, *QSAR & Comb. Sci.*, 2007, **26**, 1274-1279.
20. G. C. H. Chiang and T. Olsson, *Org. Lett.*, 2004, **6**, 3079-3082.
21. H. Firouzabadi, N. Iranpoor, M. Gholinejad and J. Hoseini, *Adv. Synth. Catal.*, 2011, **353**, 125-132.
22. H. Firouzabadi, N. Iranpoor, M. Gholinejad, S. Akbari and N. Jeddi, *RSC Advances*, 2014, **4**, 17060-17070.
23. H. Mahmoudi, A. A. Jafari, S. Saeedi and H. Firouzabadi, *RSC Advances*, 2015, **5**, 3023-3030.
24. H. Mahmoudi and A. A. Jafari, *ChemCatChem*, 2013, **5**, 3743-3749.
25. M. Gholinejad and H. Firouzabadi, *New J. Chem.*, 2015, **39**, 5953-5959.
26. H. Firouzabadi, N. Iranpoor, M. Gholinejad, S. Akbari and N. Jeddi, *RSC Adv.*, 2014, **4**, 17060-17070.
27. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst and R. N. Muller, *Chem. Rev.*, 2008, **108**, 2064-2110.
28. C. Fang and M. Zhang, *J. Mater. Chem.*, 2009, **19**, 6258-6266.
29. W. Wu, Q. He and C. Jiang, *ChemInform*, 2009, **40**, i.
30. Y. L. Jinwoo Lee, Jong Kyu Youn, Hyon Bin Na, Taekyung Yu, Hwan Kim,, Y.-M. K. Sang-Mok Lee, Ja Hun Kwak, Hyun Gyu Park, Ho Nam Chang, and J.-G. P. Misun Hwang, Jungbae Kim, and Taeghwan Hyeon, *small*, 2008, **4**, 143-152.
31. Y.-J. Song, C.-Y. Yoo, J.-T. Hong, S.-J. Kim, S.-U. Son and H.-Y. Jang, *Bull. Korean Chem. Soc.*, 2008, **29**, 1561-1564.
32. E. Ozkal, S. Özçubukçu, C. Jimeno and M. A. Pericas, *Catal. Sci. Tech.*, 2012, **2**, 195-200.
33. B. S. Lee, M. Yi, S. Y. Chu, J. Y. Lee, H. R. Kwon, K. R. Lee, D. Kang, W. S. Kim, H. B. Lim and J. Lee, *Chem. Commun.*, 2010, **46**, 3935-3937.
34. S. Kale, S. Kahandal, S. Disale and R. Jayaram, *Curr. Chem. Lett.*, 2012, **1**, 69-80.
35. F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *J. Org. Chem.*, 2011, **76**, 8394-8405.
36. I. Jlalia, C. Beauvineau, S. Beauvière, E. Önen, M. Aufort, A. Beauvineau, E. Khaba, J. Herscovici, F. Meganem and C. Girard, *Molecules*, 2010, **15**, 3087-3120.
37. P. Li, L. Wang and Y. Zhang, *Tetrahedron*, 2008, **64**, 10825-10830.

A novel and recoverable Cu(II)/ 2-aminobenzenthiol complex immobilized on magnetite/silica nanoparticles catalyzed synthesis of 1,2,3- triazole derivatives in *green* media.