

Catalysis

Super Paramagnetic, MCM-41-Supported, Recyclable Copper-Complexed Dendrimer: A Novel Nanostructured Catalyst for Propargylamine Synthesis Under Solvent-Free Conditions

Najmeh Gharibpour,^[a] Mohammad Abdollahi-Alibeik,^{*[a]} and Ali Moaddeli^[a, b]

A super paramagnetic MCM-41 with dendrites copper complex is prepared and characterized using FT-IR, BET, AAS, TEM, CV, TGA, X-ray and VSM. The catalyst was used in C–H activation reaction for the synthesis of propargylamines by the reaction of

aldehydes, amines and phenylacetylene under solvent-free conditions. Finally the catalyst was separated using an external magnet and reused many times.

1. Introduction

Propargylamine is an important moiety in diverse biologically active natural materials, and can be utilized as a key intermediate for the synthesis of several bioactive compounds.^[1] Propargylamine derivatives have also been used as starting materials for the synthesis of heterocycles such as pyrroles,^[2] quinolones,^[3] phenanthrolines,^[4] pyrrolidines,^[5] indolizines,^[6] and oxazolidinones.^[7]

Three important methodologies have been introduced for the preparation of propargylamines: 1) Nucleophilic addition of metal acetylides to enamines and imines,^[8] 2) amination of propargylic electrophiles (such as halides, propargylic phosphates and propargylic triflates)^[9] and 3) three-component coupling reaction via C–H activation (Mannich condensation). Due to furnish complex molecules from simple commercially available starting materials, three-component condensation of terminal alkynes, amines and aldehydes is certainly the most popular and efficient method among the synthetic methodologies. Additionally, this type of reaction is performed in an atom economical approach and environmentally friendly pathway through a catalytic process. Various catalytic systems such as copper,^[10] gold,^[11] indium^[12] and iron^[13] based catalysts, have been introduced in this methodology. Some of these methods

suffer from various limitations, such as application of toxic solvents and expensive non-reusable catalyst.

In recent years, heterogeneous catalysts because of their particular advantages, such as ease of separation and reusability have gained a lot of attention^[14].

Nano catalysts have a large surface to volume ratio respect to bulky materials and offer an attractive alternative to conventional catalysts.^[15] In spite of several advantages of nano catalysts over conventional catalyst systems, isolation and recovery of these very tiny species from the reaction mixture is not easy.^[16] Conventional techniques such as filtration are not efficient because of the nano size of the catalyst particles. To overcome this issue, the use of magnetic nanoparticles has emerged as a viable solution. The insoluble and paramagnetic nature of these nanoparticles provide an opportunity for easy and efficient separation of the catalysts from the reaction mixture using an external magnet.^[17]

MCM-41 is a members of mesoporous silica,^[18] which has been applied as both heterogeneous catalyst and catalyst support in many organic transformations.^[19] This compound possesses uniform tubular channels with two dimensional hexagonal structure, regular pore diameters and high surface area (more than 1000 m²/g).^[19a,d] These features allow the channels to act as nanoreactor for the desired reaction. Due to the weak catalytic activity, surface modification of MCM-41 is a useful way to promote its catalytic activity. Among the modified MCM-41 catalysts, transition metal modified MCM-41 such as V,^[20] Fe,^[21] Cu,^[22] Mn,^[23] Co,^[24] Ni^[25] and Mo^[26] have been known as powerful heterogeneous catalysts in organic reactions.

Carbon-Carbon bond coupling reactions are one of the most significant processes in organic chemistry, in order to building complex molecules from simple ones. Transition metal catalyzed C–C bond formation via C–H bond activation has attracted great interest by organic chemists in recent years.^[27] C–H activation has been carried out by various homogeneous or heterogeneous catalysts including transition metal such as

[a] N. Gharibpour, Prof. M. Abdollahi-Alibeik, Dr. A. Moaddeli
Department of Chemistry
Yazd University
Yazd 89158—13149, Iran
Tel.: +98-35-31232659
fax: +98-35-38210644
E-mail: abdollahi@yazd.ac.ir
moabdollahi@gmail.com

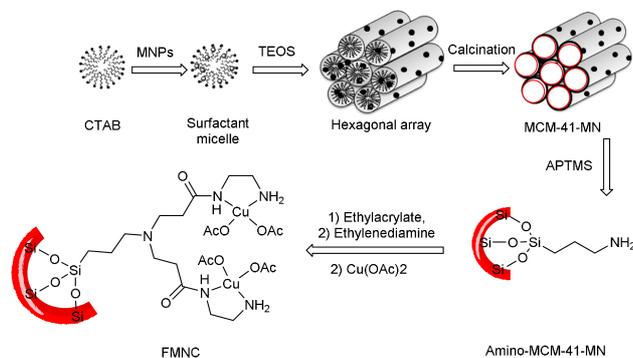
[b] Dr. A. Moaddeli
Legal Medicine Research Center
Legal Medicine Organization of Iran
Tehran, Iran

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/slct.201700180>

zinc,^[28] silver,^[29] gold,^[30] nickel,^[31] copper(I),^[32] copper(II),^[33] iron oxide,^[34] bismuth,^[35] iridium,^[36] cobalt^[37] and indium.^[38]

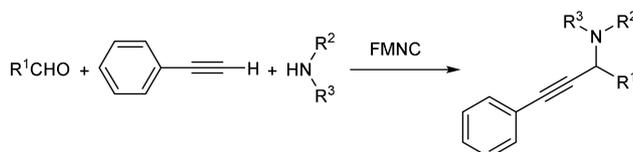
Copper is a cheap, efficient, and non-toxic component and used in a wide range of heterogeneous and homogeneous catalytic systems for the synthesis of various organic molecules, particularly through C–H bond activation and subsequent C–C bond formation.^[39] Heterogeneous copper catalysts with different supports such as copper(II)pybox complex under high-vibration ball-milling,^[40] copper nanoparticles supported on starch micro particles,^[41] oxidized copper nanoparticles on titania,^[42] impregnated copper on magnetite,^[43] Cu-nanoparticles stabilized on modified montmorillonite,^[44] mesoporous copper-aluminum based nanocomposites,^[45] lanthanum loaded CuO nanoparticles,^[46] a sulfonate-based Cu^I metal-organic framework,^[47] magnetic CuO nanoparticles supported on graphene oxide,^[48] Cu/C nanoparticles^[49] and copper modified MCM-41 nano particles^[50] are reported for preparation of propargylamines

In this research, Cu^{II} complex of dendrimer ligands on the modified MCM-41 (Scheme 1) is synthesized and reported as a



Scheme 1. Schematic illustration of reaction sequences for the preparation of FMNC and its possible structure.

new magnetically recoverable catalyst (FMNC) for the synthesis of propargylamines by one-pot three component reaction of phenylacetylene, amines and aldehydes (Scheme 1). To the extent of our knowledge, this is the first report for the application of this type of the catalyst in the C–H bond activation.

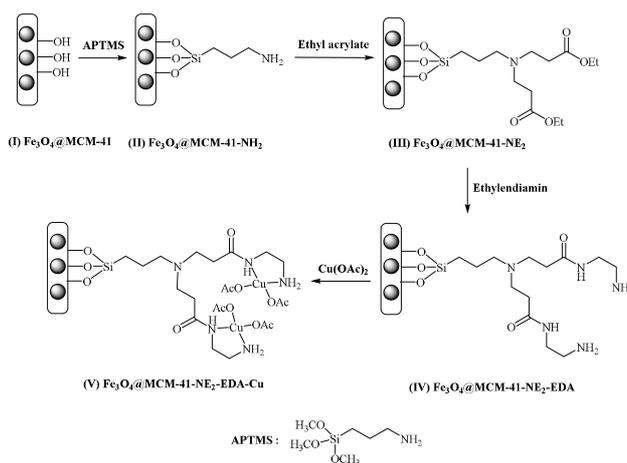


Scheme 2. Synthesis of propargylamines using FMNC catalyst.

2. Result and discussion

2.1. Catalyst

The catalyst was prepared by consecutive functionalization reaction on the Fe₃O₄@MCM-41. Dendrimer core (Fe₃O₄@MCM-41-NH₂) was prepared by the reaction of Fe₃O₄@MCM-41 with 3-aminopropyltrimethoxysilane (APTMS). Dendrimer ligand was obtained by subsequent reaction of Fe₃O₄@MCM-41-NH₂ with ethyl acrylate and ethylenediamine, respectively. The dendrite complex (Fe₃O₄@MCM-41-NE₂-EDA-Cu) was prepared by the reaction of ligand with copper(II) acetate (Scheme 3).



Scheme 3. Catalyst preparation.

2.2. The catalyst characterization

The FT-IR spectra of various steps of catalyst synthesis are shown in Figure 1. Fe₃O₄@MCM-41 shows characteristic peaks at 1240, 1082 and 806 cm⁻¹ corresponding to stretching Si–O–Si and the peak at 461 cm⁻¹ linked to bending Si–O–Si. In this spectrum the bands at 585 and 630 cm⁻¹ linked to the Fe–O bonds are also observed (Figure 1a). In the spectrum of Fe₃O₄@MCM-41-NH₂ apart from the main peaks of Fe₃O₄@MCM-41, the peaks at 1495 and 1560 cm⁻¹ linked to bending aliphatic CH and NH, confirm that Fe₃O₄@MCM-41 surface is modified by APTMS (Figure 1b). Fe₃O₄@MCM-41-NE₂ spectrum shows carbonyl peak of ester at 1738 cm⁻¹ (Figure 1c). The carbonyl peak of amide appeared at 1654 cm⁻¹ in Fe₃O₄@MCM-41-NE₂-EDA spectrum (Figure 1d). After copper complex formation in FMNC, the carbonyl peak of amide shifts to 1647 cm⁻¹ (Figure 1e).

The low angle XRD patterns of MCM-41, Fe₃O₄@MCM-41 and FMNC are shown in Figure 2. MCM-41 shows a strong peak at 2θ = 2.4° linked to the characteristic of ordered hexagonal and two other characteristic peaks of MCM-41 at 2θ = 4.0° and 4.6°, assigned to reflections at (100), (110) and (200), respectively (Figure 2a), which match well with those reported in the literature for hexagonal mesoporous silica materials (JCPDS no. 00–049–1711). In the low angle XRD pattern of Fe₃O₄@MCM-41

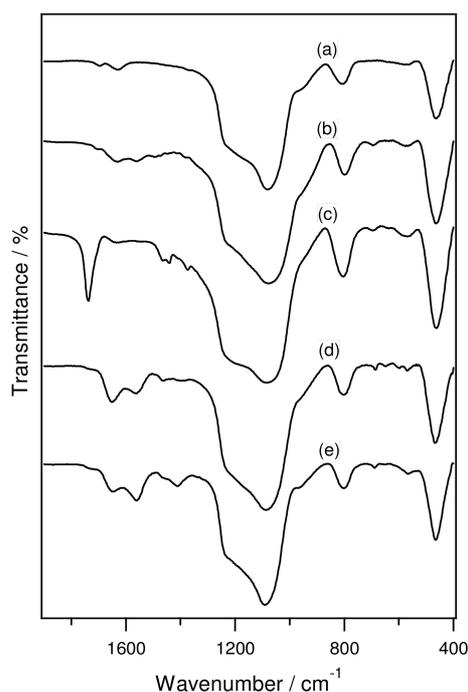


Figure 1. FT-IR spectra of a) Fe_3O_4 @MCM-41, b) Fe_3O_4 @MCM-41- NH_2 , c) Fe_3O_4 @MCM-41- NE_2 , d) Fe_3O_4 @MCM-41- NE_2 -EDA, e) FMNC.

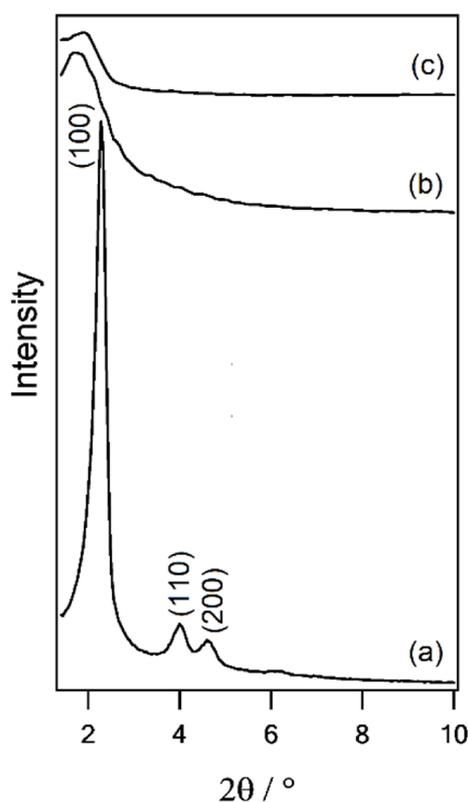


Figure 2. Low angle XRD pattern of a) MCM-41, b) Fe_3O_4 @MCM-41 and c) FMNC.

the decrease in the main peak intensity, and the increase in its width indicate the decrease of order of hexagonal mesostructures due to incorporation of Fe_3O_4 into the network of MCM-41 (Figure 2b).

Due to the incorporation of Fe_3O_4 , an increase in the d-spacing (a decrease in 2θ according to the Bragg's equation) and unit-cell parameters are also observed (Table 1). The former

Entry	Sample	2θ (°)	d-spacing (nm) ^a
1	MCM-41	2.4	3.8
2	Fe_3O_4 @MCM-41	1.72	5.1
3	FMNC	1.9	4.7

^a $d_{100} = n\lambda / 2\sin\theta$, ($n=1$, Fix λ (Cu $k\alpha$) = 1.54 Å)

result is probably due to the partial replacement of the Si by the Fe ion, resulting in collapse of the ordered hexagonal structure of MCM-41. The increase in unit-cell parameters after Fe_3O_4 incorporation is probably related to the larger size of Fe compared to Si.

Occupation of hexagonal mesoporous cavities by dendrimer/copper complex has led to a decrease in intensity of the main peak and shift to the higher angle ($2\theta = 1.9^\circ$) in the low angle XRD pattern of FMNC. Moreover, the cavity occupation causes an increase in the d-spacing compared to Fe_3O_4 @MCM-41 that often is seen in mesoporous silica compounds.

The high angle XRD pattern of FMNC in Figure 3d displays weak peaks at $2\theta = 30, 36, 43, 57, 63$ and 74° assigned to

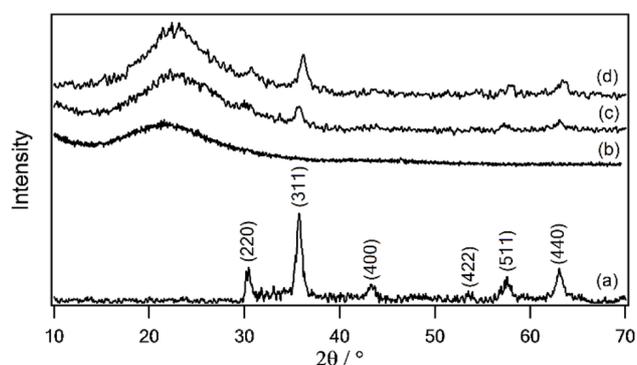


Figure 3. High angle XRD pattern of a) Fe_3O_4 , b) MCM-41, c) Fe_3O_4 @MCM-41, d) FMNC.

reflections at (220), (311), (400), (422), (511), (440), which match well with those reported in the literature for Fe_3O_4 (JCPDS no. 72-2303). These results are compatible to the observed peaks of Fe_3O_4 @MCM-41 (Figure 3c) and the pure Fe_3O_4 (Figure 3a). The low intensity of main peaks of Fe_3O_4 is because of the low molar ratio of Fe_3O_4 in the support (Si/Fe = 119/1).

Studying the mesostructure of the fresh FMNC by TEM (Figure 4) shows a clear porosity (Figure 4a) and ordered

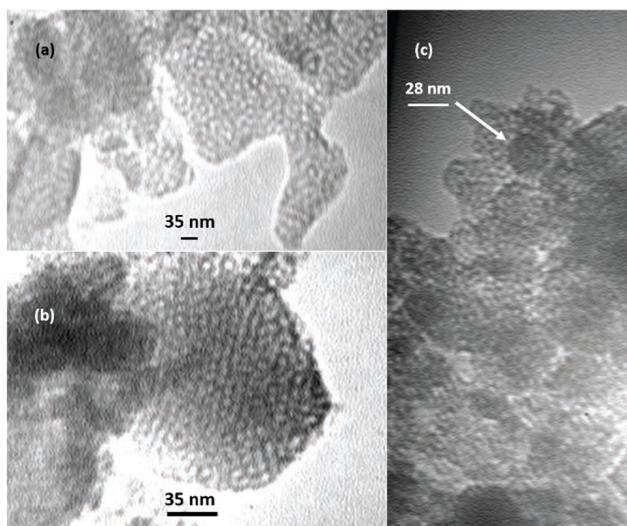


Figure 4. TEM image of FMNC.

mesostructured channels (Figure 4b). Partial disorder of mesoporous system is related to the dispersion of Fe_3O_4 into the MCM-41 framework (Figure 4c) that is confirmed by XRD data. The mesostructure of the recovered sample after last reaction was also studied by TEM (Figure 5). As shown in Figure 5,

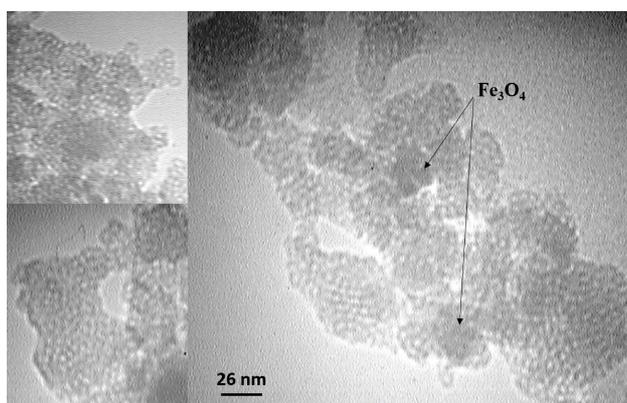


Figure 5. TEM image of recovered FMNC after last reaction cycle.

mesostructure of the catalyst is still intact and there is no agglomeration of nanoparticles.

To survey the magnetic property of Fe_3O_4 @MCM-41 and FMNC, magnetic measurements were accomplished using a room temperature VSM in an applied magnetic field. Typical super paramagnetic nature at 300 K is confirmed by not observing any hysteresis loops and also zero coercivity value for the both samples (Figure 6). The saturation magnetization value of Fe_3O_4 @MCM-41 and FMNC are 4.05 emu/g and 2.50 emu/g (Figure 6a and 6b), respectively. The observed decrease in magnetization saturation value after Fe_3O_4 @MCM-41 modification is attributed to the organic matter and the relative low

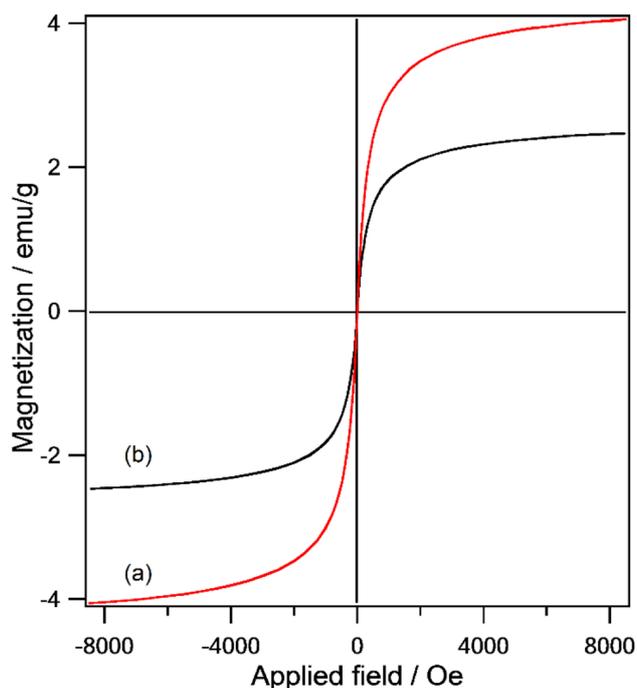


Figure 6. Magnetization curves of a) Fe_3O_4 @MCM-41, b) FMNC.

mass ratio of Fe_3O_4 in the latter sample. In addition, The FMNC can be manipulated by using external magnet for magnetic separation (Figure 7).

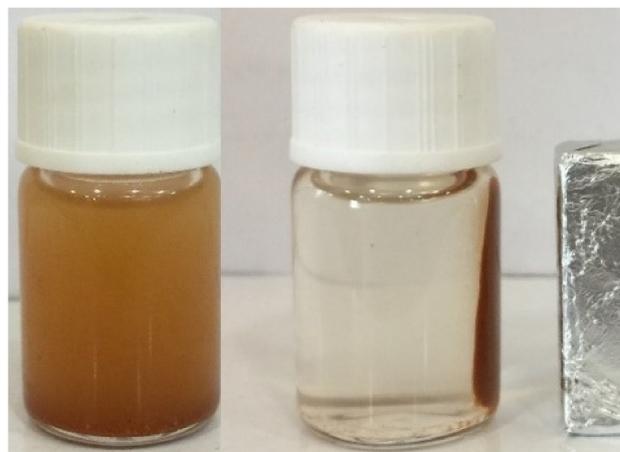


Figure 7. Magnetic separation ability of FMNC.

The textural characteristics of FMNC were investigated by N_2 adsorption-desorption isotherm. Unto the obtained results the surface area (S_{BET}), pore diameter (D_{pore}) and pore volume (V_{pore}) of Fe_3O_4 @MCM-41 are 783.24 m^2/g , 7.4 nm and 1.00 cm^3/g , respectively. In this isotherms, the mesoporous deflection is apperceived at the medium p/p° partial pressure region ($p/p^\circ = 0.2-0.4$), due to the N_2 capillary condensation in the mesopores. A sharper hysteresis is apperceived at higher p/p°

($p/p^\circ > 0.8$). The hysteresis in this region is due to the N_2 condensation within the voids formed by nanoparticles (Figure 8a). The absence of mesoporous inflection at the medium

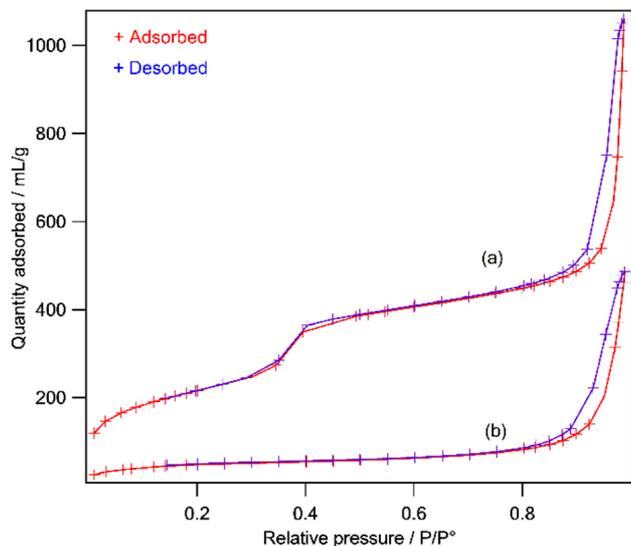


Figure 8. N_2 adsorption-desorption isotherms of a) $Fe_3O_4@MCM-41$, b) FMNC.

p/p° partial pressure region ($p/p^\circ = 0.2-0.4$) in N_2 adsorption-desorption isotherms of the FMNC catalyst (Figure 8b), confirms the grafted organic matters on the inner surface of the $Fe_3O_4@MCM-41$. In addition, the decrease in amount of S_{BET} and V_p and also increase in amount of d_p confirm the cavities filling, that are gathered in Table 2.

Table 2. Textural properties of the FMNC and $Fe_3O_4@MCM-41$				
Entry	Sample	S_{BET}^a (m^2/g)	d_p BJH ^b (nm)	V_p^c (cm^3/g)
1	$Fe_3O_4@MCM-41$	783.2	1.97	1.00
2	FMNC	175.7	2.06	0.49

^aBET Surface Area ^bPore diameter according to the maximum of the BJH desorption pore size distribution ^cSingle point adsorption total pore volume

Stability of the FMNC was evaluated using thermogravimetric analysis (TGA) by heating the sample in the range of room temperature to $800^\circ C$ (Figure 9). In the thermogravimetric curve, there are two weight loss steps between room temperature to $280^\circ C$ and $280-700$. The first weight loss step could be attributed to desorption of the physically adsorbed moisture and residual organic solvents. The second weight loss step is attributed to the removal of the organometallic dendrimer on the surface of $Fe_3O_4@MCM-41$. According to the Figure 9a, the total weight loss percent of thermogravimetric analysis is 24.4% (11.47 mg weight loss in- the 47 mg total sample weight), showing the thermal stability of organometallic

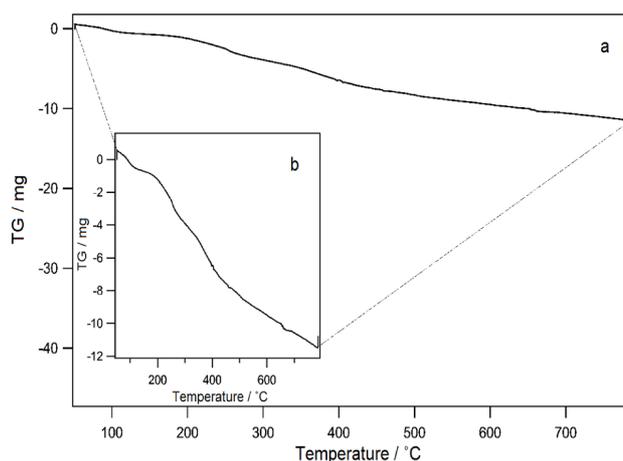


Figure 9. a) Thermogravimetric analysis of FMNC, b) magnification of FMNC thermogravimetric analysis.

dendrimer modified on the surface of $Fe_3O_4@MCM-41$ up to $280^\circ C$.

In order to identify oxidation state of Cu in the catalyst, the electrochemical properties of the copper complex in fresh and reused catalyst after cycle 2 have been studied by cyclic voltammetry (CV) in DMSO. The cyclic voltammogram is shown in Figure 10. The voltammogram of the copper(II) complex in

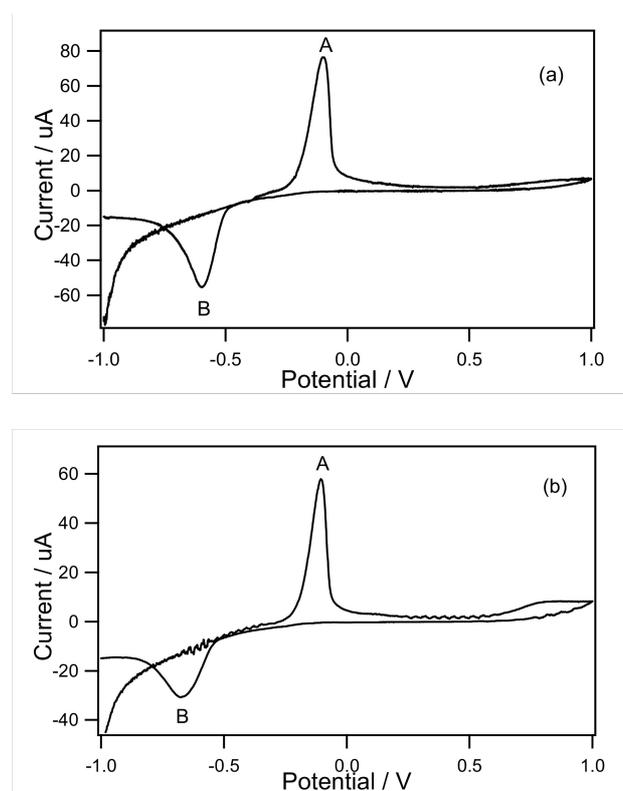
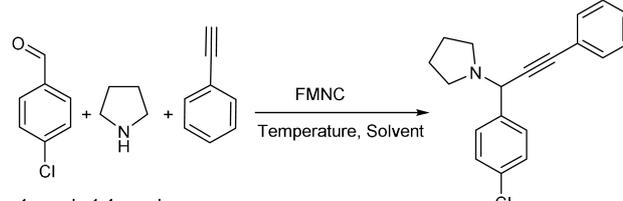


Figure 10. Cyclic voltammograms of (a) fresh FMNC, (b) reused FMNC after cycle 2.

Table 3. Optimization of reaction conditions for Propargylamines synthesis



Entry	Ligand:Cu(OAc) ₂ mass ratio (mg)	FMNC (mg)	Solvent	Phenylacetylene (mmol)	Temp (°C)	Time (min)	Yield (%) ^a
1	100:10	20	-	1.2	100	60	63
2	100:15	20	-	1.2	100	30	92
3	100:20	20	-	1.2	100	30	69
4	100:15	10	-	1.2	100	75	76
5	100:15	30	-	1.2	100	30	61
6	100:15	20	-	1.1	100	40	74
7	100:15	20	-	1.3	100	30	64
8	100:15	20	H ₂ O ^b	1.2	Reflux	180	40 ^c
9	100:15	20	EtOH ^b	1.2	Reflux	120	40 ^c
10	100:15	20	CH ₃ CN ^b	1.2	Reflux	120	30 ^c
11	100:15	20	DMF ^b	1.2	Reflux	120	50 ^c
12	100:15	20	THF ^b	1.2	Reflux	120	20 ^c
13	100:15	20	-	1.2	90	90	68
14	100:15	20	-	1.2	110	30	90
15	-	-	-	1.2	100	120	50 ^c
16	0:1.8	-	-	1.2	100	120	69
17	0:0.6	-	-	1.2	100	30	23

^aIsolated yield ^b1.0 mL ^cReaction progress monitored by TLC

fresh and reused FMNC show only an oxidation peak (Cu/Cu²⁺) at -0.1 V during the anodic potential scan (Figure 10, peak A). During the return cathodic potential scan, only a single reduction peak (Cu²⁺/Cu) is observed at -0.6 V (Figure 10, peak B).^[51] Results from electrochemical properties show that oxidation state of copper in the catalyst is (II) and this state remained unchanged in the recovered catalyst.

2.3. Catalytic activity

Synthesis of propargylamines by a three component reaction of aldehyde, phenylacetylene and amines is selected as the applicatory reaction for the study of FMNC catalytic activity.

To optimize the reaction conditions, the reaction of 4-chlorobenzaldehyde, phenylacetylene and pyrrolidine was studied as model reaction, by testing various parameters such as catalyst loading, catalyst amount, phenylacetylene amount, solvent and temperature. The effect of loading mass ratios on the catalytic activity of FMNC was studied in the model reaction at 100 °C and solvent-free condition. Results show that in terms of reaction time and yield of the product, the catalyst with loading mass ratios of ligand:Cu(OAc)₂=100:15 has the best activity (Table 3, entries 1–3).

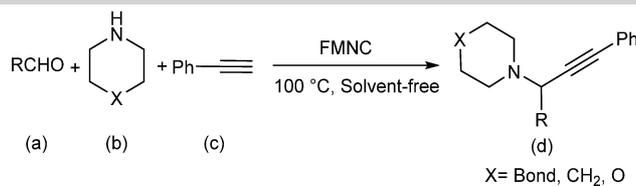
In spite of progress of reaction without catalyst (Table 3, entry 15), the effect of the catalyst amount on the catalytic activity was investigated by using the catalyst with loading mass ratios of ligand:Cu(OAc)₂=100:15 in the model reaction (Table 3, entries 2 and 4–5). Based on the results, the use of 20 mg catalyst in solvent free condition at 100 °C has the best activity. The effect of phenylacetylene amount on the catalytic

activity was studied using 20 mg catalyst with loading mass ratios of ligand:Cu(OAc)₂=100:15 in the model reaction with different phenylacetylene amounts (Table 3, entries 2, 6 and 7), and results show that the use of 1.2 mmol phenylacetylene in solvent-free condition at 100 °C has the best result. The effect of solvent on the catalytic activity was studied by using 20 mg catalyst with loading mass ratios of ligand:Cu(OAc)₂=100:15 in the model reaction with various solvents (Table 3, entries 2 and 8–12). Considering the yield of product and reaction time, it is concluded that solvent-free condition at 100 °C has the best result. The effect of reaction temperature on the catalytic activity was studied by using 20 mg catalyst with loading mass ratios of ligand:Cu(OAc)₂=100:15 in the model reaction at solvent-free condition (Table 3, entries 2, 13 and 14). The best result was obtained at 100 °C. Increasing the reaction temperature up to 110 °C causes a decrease in the yield of product and increasing of the amount of by-products.

To investigate efficiency of support on the catalytic activity of Cu²⁺, the model reaction was carried out in the presence of 0.9 mol% copper (equal to the total Cu mol% in 20 mg of fresh FMNC catalyst) using 1.8 mg Cu(OAc)₂. The reaction was completed after 120 min and yield of the product was found to be 69% (Table 3, entry 16) while, the model reaction in the presence of 20 mg FMNC at similar condition was completed after 30 min and yield of the product was obtained 92%, without byproduct.

In order to investigate the nature of the catalyst (homogeneous or heterogeneous), and check whether the leached Cu during catalytic process can catalyzed reaction homogeneously or not, the model reaction was carried out in the presence of

Table 4. Propargylamines synthesis by three-component coupling of aldehydes, alkynes and secondary amines catalyzed by FMNC



Entry	Aldehyde	Amine	Product	Time (min) ^a	Yield (%) ^b
1				30	92
2				70	92
3				30	90
4				35	85
5				15	97
6				40	92
7				25	91
8				35	94
9				130	93

Table 4. continued

Entry	Aldehyde	Amine	Product	Time (min) ^a	Yield (%) ^b
10				60	84
11				45	92
12				105	89
13				30	91
14				120	88

^aReaction completion monitored by TLC ^bIsolated yield ^cGeneral procedure for the synthesis of products: aldehyde (1 mmol), pyrrolidine (1.4 mmol), phenylacetylene (1.2 mmol), FMNC (20 mg, 0.9 mol% copper) as catalyst in the solvent free condition at 100 °C.

Table 5. Reusability of FMNC as a catalyst in propargylamine synthesis

Entry	Catalyst amount (mg)	Cu mol% before reaction	Yield (%) ^a	Time (min) ^b	Cu mol% after reaction
1	20	0.9	92	30	0.56
2	20	0.56	89	50	0.36
3	20	0.36	87	70	0.31

General procedure for reusability study: 4-Chlorobenzaldehyde (1 mmol), pyrrolidine (1.4 mmol), phenylacetylene (1.2 mmol), FMNC (20 mg, 0.9 mol%) as catalyst in the solvent free condition at 100 °C.
^aIsolated yield. ^bReaction completion monitored by TLC.

0.34 mol% copper (equal to the total Cu mol% leached in 20 mg fresh FMNC catalyst after first run) using 0.6 mg Cu(OAc)₂. After 30 min, reaction was worked up and only 23% of product was separated and 54% of 4-chlorobenzaldehyde was recovered. However, leached Cu²⁺ in the presence of heterogeneous catalyst may have a smaller role (even less than 23% yield) in the progress of the reaction due to higher rate of the reaction in the presence of heterogeneous catalyst.

The optimized condition was applied for the preparation of many propargylamine derivatives by the reaction of various types of aldehydes with both electron-donating and electron-withdrawing substituents, phenylacetylene and various amines (Table 4). Halides substituents have a significant effect on the activity of benzaldehyde (F > Cl > Br), and pyrrolidine has the most activity among the other used amines such as piperidine and morpholine.

Table 6. The comparative study of the activity of fresh FMNC and recycled catalyst

Entry	Catalyst	Temp (°C)	Solvent	Cu (mol%)	Time (h)	Yield (%) ^a	Yield (%) ^b	Ref.
1	FMNC	100	-	0.9	0.5	92	87	This work
2	MNP@PILAu	60	H ₂ O	1.0	12	97	91	[52]
3	Cu-MCM-41	100	-	2.9	2	85	77	[50]
4	Ag-G	40	CH ₂ Cl ₂	0.1	24	82	-	[53]
5	CuNPs@MS	60	THF	0.3	20	96	95	[54]

^aIsolated yield ^bIsolated yield for the various model reactions in the presence of recycled catalyst

In order to investigate the reusability of the catalyst, the separated catalyst by an external magnet, washed by CHCl₃ (3 × 3 mL) and dried at 60 °C for 1 h, then reused in the model reaction at same reaction (Table 5). Considering the time and yield of the reaction, a moderate deactivation of the catalyst can be observed because of copper leaching from the catalyst. To investigate this issue, the Cu loading of the recovered catalyst from second cycle was determined by atomic absorption spectroscopy (Table 5, entry 3). The percentage of loaded copper on the catalyst (0.31 mol%) confirms the leaching and consequently deactivation of the catalyst (65% of Cu leaching) (Table 5, the difference between entries 1 and 3).

We report a comparative study of the activity of FMNC with other reported heterogeneous metal containing catalysts for the preparation of propargylamine derivatives through A³ coupling reaction of aldehyde, amine, and phenylacetylene using metal-based catalysts (Table 6). With an overview of Table 6, the comparative study shows that presented catalyst is comparable to other catalytic systems in term of reaction time and yield of the product. In addition, moderate reaction temperature, lack of usage of an inert atmosphere, and solvent-free condition are other advantages of our method. The catalytic activity of recycled FMNC catalysts was also compared with other heterogeneous catalysts of Table 6. The decline in the isolated yield of product after third run of FMNC is comparable with the same results for other catalysts (Table 6).

3. Conclusion

Finally, we have presented a new magnetically recyclable catalyst with magnetite core and dendrimer copper complex (Fe₃O₄@MCM-41-NE₂-EDA-Cu (FMNC), Si:Fe₃O₄ = 40:1, loading mass ratio of ligand:Cu(OAc)₂ = 100:15). The catalyst is efficient in the synthesis of propargylamine synthesis by three-component reaction of aldehyde, phenylacetylene and secondary amine. The catalyst was recycled several times with mild decrease in activity and without decrease in magnetic properties. High products yields, very simple workup and easy recovery catalyst are some advantages of this catalyst.

Supporting Information

Experimental procedure for the preparation of FMNC catalyst and propargylamines and also the FT-IR, ¹H/¹³C NMR spectra of the products can be found in the supporting information.

Acknowledgement

We are thankful to the research council of Yazd University for financial support of this research.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–H activation reaction · dendrimeric copper-complex · Nanostructured catalyst · propargylamine · super paramagnetic MCM-41

- [1] a) F. N. Shirota, E. G. DeMaster, H. T. Nagasawa, *J. Med. Chem.* **1979**, *22*, 463–464; b) P. H. Yu, B. A. Davis, A. A. Boulton, *J. Med. Chem.* **1992**, *35*, 3705–3713.
- [2] Y. Yamamoto, H. Hayashi, T. Saigoku, H. Nishiyama, *J. Am. Chem. Soc.* **2005**, *127*, 10804–10805.
- [3] F. Xiao, Y. Chen, Y. Liu, J. Wang, *Tetrahedron* **2008**, *64*, 2755–2761.
- [4] D. Shibata, E. Okada, J. Molette, M. Médebielle, *Tetrahedron Lett.* **2008**, *49*, 7161–7164.
- [5] D. F. Harvey, D. M. Sigano, *J. Org. Chem.* **1996**, *61*, 2268–2272.
- [6] B. Yan, Y. Liu, *Org. Lett.* **2007**, *9*, 4323–4326.
- [7] E.-S. Lee, H.-S. Yeom, J.-H. Hwang, S. Shin, *Eur. J. Org. Chem.* **2007**, *2007*, 3503–3507.
- [8] a) C. Wei, C.-J. Li, *J. Am. Chem. Soc.* **2002**, *124*, 5638–5639; b) C. Fischer, E. M. Carreira, *Org. Lett.* **2001**, *3*, 4319–4321.
- [9] Y. Imada, M. Yuasa, I. Nakamura, S.-I. Murahashi, *J. Org. Chem.* **1994**, *59*, 2282–2284.
- [10] a) M. J. Albaladejo, F. Alonso, Y. Moglie, M. Yus, *Eur. J. Org. Chem.* **2012**, *2012*, 3093–3104; b) X. Tang, J. Kuang, S. Ma, *Chem. Commun.* **2013**, *49*, 8976–8978; c) M. Abdollahi-Alibeik, A. Moaddeli, *RSC Adv.* **2014**, *4*, 39759–39766; d) Z. Lin, D. Yu, Y. Zhang, *Tetrahedron Lett.* **2011**, *52*, 4967–4970.
- [11] a) L. F. Bobadilla, T. Blasco, J. A. Odriozola, *Phys. Chem. Chem. Phys.* **2013**, *15*, 16927–16934; b) B. Karimi, M. Gholinejad, M. Khorasani, *Chem. Commun.* **2012**, *48*, 8961–8963; c) C. Wei, C.-J. Li, *J. Am. Chem. Soc.* **2003**, *125*, 9584–9585.
- [12] J. S. Yadav, B. V. Subba Reddy, A. V. Hara Gopal, K. S. Patil, *Tetrahedron Lett.* **2009**, *50*, 3493–3496.
- [13] B. Sreedhar, A. S. Kumar, P. S. Reddy, *Tetrahedron Lett.* **2010**, *51*, 1891–1895.
- [14] N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199–218.
- [15] a) P. Munnik, P. E. de Jongh, K. P. de Jong, *Chem. Rev.* **2015**, *115*, 6687–6718; b) A. Z. Moshfegh, *J. Phys. D: Appl. Phys.* **2009**, *42*, 233001.
- [16] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, *Chem. Rev.* **2011**, *111*, 3036–3075.
- [17] M. Abdollahi-Alibeik, A. Rezaeipoor-Anari, *J. Magn. Magn. Mater.* **2016**, *398*, 205–214.
- [18] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712.
- [19] a) M. Abdollahi-Alibeik, A. Rezaeipoor-Anari, *Cat. Sci. Tech.* **2014**, *4*, 1151–1159; b) M. Abdollahi-Alibeik, A. Moaddeli, *New J. Chem.* **2015**, *39*, 2116–

- 1222; c) M. Abdollahi-Alibeik, E. Shabani, *J. Iranian Chem. Soc.* **2013**, *11*, 351–359; d) M. Abdollahi-Alibeik, M. Pouriyaevali, *Catal. Commun.* **2012**, *22*, 13–18; e) M. Abdollahi-Alibeik, E. Heidari-Torkabad, *C. R. Chim.* **2012**, *15*, 517–523; f) R. Nejat, A. R. Mahjoub, Z. Hekmatian, T. Azadbakht, *RSC Adv.* **2015**, *5*, 16029–16035.
- [20] F. Farzaneh, E. Zamanifar, C. D. Williams, *J. Mol. Catal. A: Chem.* **2004**, *218*, 203–209.
- [21] J.-S. Choi, S.-S. Yoon, S.-H. Jang, W.-S. Ahn, *Catal. Today* **2006**, *111*, 280–287.
- [22] L. Wang, A. Kong, B. Chen, H. Ding, Y. Shan, M. He, *J. Mol. Catal. A: Chem.* **2005**, *230*, 143–150.
- [23] S. Vetrivel, A. Pandurangan, *J. Mol. Catal. A: Chem.* **2005**, *227*, 269–278.
- [24] V. Cortés Corberán, M. J. Jia, J. El-Haskouri, R. X. Valenzuela, D. Beltrán-Porter, P. Amorós, *Catal. Today* **2004**, *91–92*, 127–130.
- [25] Á. Szegedi, M. Popova, V. Mavrodinova, M. Urbán, I. Kiricsi, C. Minchev, *Microporous Mesoporous Mater.* **2007**, *99*, 149–158.
- [26] S. Higashimoto, Y. Hu, R. Tsumura, K. Iino, M. Matsuoka, H. Yamashita, Y. G. Shul, M. Che, M. Anpo, *J. Catal.* **2005**, *235*, 272–278.
- [27] V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770.
- [28] a) P. B. Sarode, S. P. Bahekar, H. S. Chandak, *Synlett* **2016**, *6*, 3117–3125. b) T. R. Mandlimath, K. I. Sathiyarayanan, *RSC Adv.* **2016**, *6*, 3117–3125.
- [29] N. Salam, A. Sinha, A. S. Roy, P. Mondal, N. R. Jana, S. M. Islam, *RSC Adv.* **2014**, *4*, 10001.
- [30] C. Wei, C.-J. Li, *J. Am. Chem. Soc.* **2003**, *125*, 9584–9585.
- [31] K. Namitharan, K. Pitchumani, *Eur. J. Org. Chem.* **2010**, *2010*, 411–415.
- [32] H. Naeimi, M. Moradian, *App. Catal. A: Gen.* **2013**, *467*, 400–406.
- [33] X. Liu, B. Lin, Z. Zhang, H. Lei, Y. Li, *RSC Adv.* **2016**, *6*, 94399–94407.
- [34] a) P. Mandal, A. P. Chattopadhyay, *Dalton Trans.* **2015**, *44*, 11444–11456; b) D. Bhuyan, M. Saikia, L. Saikia, *Catal. Commun.* **2015**, *58*, 158–163.
- [35] A. Teimouri, A. N. Chermahini, M. Narimani, *Bull. Korean Chem. Soc.* **2012**, *33*, 1556–1560.
- [36] C. Fischer, E. M. Carreira, *Org. Lett.* **2001**, *3*, 4319–4321.
- [37] C.-J. Li, W.-W. Chen, H.-P. Bi, *Synlett* **2010**, *2010*, 475–479.
- [38] C. Y. K. Chan, N.-W. Tseng, J. W. Y. Lam, J. Liu, R. T. K. Kwok, B. Z. Tang, *Macromolecules* **2013**, *46*, 3246–3256.
- [39] S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, *Chem. Rev.* **2013**, *113*, 6234–6458.
- [40] Z. Li, Z. Jiang, W. Su, *Green Chem.* **2015**, *17*, 2330–2334.
- [41] M. Gholinejad, F. Saadati, S. Shaybanizadeh, B. Pullithadathil, *RSC Adv.* **2016**, *6*, 4983–4991.
- [42] M. J. Albaladejo, F. Alonso, Y. Moglie, M. Yus, *Eur. J. Org. Chem.* **2012**, *2012*, 3093–3104.
- [43] M. J. Aliaga, D. J. Ramon, M. Yus, *Org. Biomol. Chem.* **2010**, *8*, 43–46.
- [44] B. J. Borah, S. J. Borah, L. Saikia, D. K. Dutta, *Cat. Sci. Tech.* **2014**, *4*, 1047–1054.
- [45] J. Dulle, K. Thirunavukkarasu, M. C. Mittelmeijer-Hazeleger, D. V. Andreeva, N. R. Shiju, G. Rothenberg, *Green Chem.* **2013**, *15*, 1238.
- [46] R. Sasikala, S. K. Rani, D. Easwaramoorthy, K. Karthikeyan, *RSC Adv.* **2015**, *5*, 56507–56517.
- [47] P. Li, S. Regati, H.-C. Huang, H. D. Arman, B.-L. Chen, J. C.-G. Zhao, *Chin. Chem. Lett.* **2015**, *26*, 6–10.
- [48] M. Mirabedini, E. Motamedi, M. Z. Kassaee, *Chin. Chem. Lett.* **2015**, *26*, 1085–1090.
- [49] H. Sharghi, R. Khalifeh, F. Moeini, M. Beyzavi, A. S. Beni, M. Doroodmand, *J. Iranian Chem. Soc.* **2011**, *8*, S89–S103.
- [50] M. Abdollahi-Alibeik, A. Moaddeli, *RSC Adv.* **2014**, *4*, 39759.
- [51] G. J. Pyrka, R. J. Seeney, A. A. Pinkerton, *Acta Crystallogr. Sec. C: Cryst. Struct. Commun.* **1991**, *47*, 510–513.
- [52] F. M. Moghaddam, S. E. Ayati, S. H. Hosseini, A. Pourjavadi, *RSC Adv.* **2015**, *5*, 34502–34510.
- [53] N. Salam, A. Sinha, A. S. Roy, P. Mondal, N. R. Jana, S. M. Islam, *RSC Adv.* **2014**, *4*, 10001–10012.
- [54] M. Gholinejad, F. Saadati, S. Shaybanizadeh, B. Pullithadathil, *RSC Adv.* **2016**, *6*, 4983–4991.

Submitted: January 30, 2017

Revised: March 29, 2017

Accepted: March 31, 2017