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Bimetallic Ni/Cu mesoporous silica nanoparticles as an efficient and reusable catalyst for the Sonogashira cross-coupling reactions

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ABSTRACT

A bimetallic mesoporous system (Ni/Cu-MCM-41) has been developed and evaluated as an efficient catalyst for the Sonogashira cross-coupling reaction, under palladium-free conditions. In this new methodology, a wide range of aryl halides react with phenylacetylene to give the corresponding disubstituted alkynes in good yields. Moreover, the present catalytic system is desired because of its high efficiency, easy preparation, low cost, high activity, and good recyclability.

1. Introduction

Carbon–carbon coupling reactions are valued in synthetic chemistry for their usage in setting up the carbon skeleton of organic molecules. Among them, the Sonogashira cross-coupling is a straightforward method for forming of C(sp)-C(sp^2) bonds between terminal alkynes and aryl halides [1–4]. This methodology, was first reported by Kenkichi Sonogashira in 1975 [5]. The Sonogashira reaction is an effective style for creation of arylalkynes and alkenynes which are substantial moieties in the synthesis of biologically active molecules, pharmaceuticals, agrochemicals, polymers, and engineered materials [6–9]. These compounds are employed in optical materials, sensing, and molecular electronics [10–13]. Therefore, finding the convenient synthetic methodologies for the Sonogashira cross-coupling reaction is an aim of great interest. Traditionally the cross-coupling reactions have been performed using different palladium catalysts [14–17]. It should be noted that in spite of significant prospects of palladium catalysts in coupling reactions, some limitations including the high cost and possible toxicity of palladium in these processes have become a crucial challenge. So, development of alternative ways with a better environment friendly and non-toxic catalytic system has been stimulated in recent years. In this context, researchers have devoted much effort to focus on using of metals cheaper than palladium. Therefore, various methodologies have been reported in the literature for the Sonogashira cross-coupling reactions catalyzed by nickel and copper, due to the lower cost and easy availability of these metals [18–29]. However, the use of Cu as a co-catalyst raises several drawbacks such as generation of homocoupling products of the terminal alkyne due to the use of an extra environmentally-unfriendly chemical (CuX). In this regard, a Sonogashira cross-coupling protocol that allows the exclusion of copper additives is highly desirable [30–33]. In recent decades, bimetallic catalysts as an important class of active catalysts have attracted much of attention in academic and industrial applications [34]. These components display new properties with respect to the monometallic systems. Indeed, the presence of two metals enhances activity and selectivity of the catalyst, caused by the electronic and structural interactions and synergistic effects between them. Therefore, this perspective highlights an alternative pattern for the use of bimetallic catalysts in coupling reactions [35–38]. Nowadays, finding catalyst supports is one of challenges in sustainable chemistry to design new heterogeneous catalysts. Due to advantages of mesoporous materials such as porosity, high thermal stability, and high specific surface, they are appropriate candidates for synthesis of transition metal supported catalysts [25,39,40]. Keeping this in mind, Herein, we have focused our attention on the influence and use of mesoporous bimetallic catalysts in C–C coupling reactions. So, we report Ni/Cu-MCM-41 as a simple and efficient catalyst for the Sonogashira cross-coupling reaction between phenylacetylene and aryl halides in the synthesis of phenylethynyl derivatives under palladium-free conditions (Scheme 1).

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2. Experimental

2.1. Material and instrumentation

Fourier transform infrared (FT-IR) spectra are recorded by a Nicolet IR-100 infrared spectrometer using KBr pellets in the range 400–4000 cm^{-1}. The nuclear magnetic resonance (NMR) spectra are recorded using a Brucker DRX 300-Avance spectrometer, operating at 300 and 75 MHz in $CDCl_3$ as solvent in the presence of tetramethylsilane (TMS) as internal standard. X-ray powder diffraction (XRD) is performed using Philips XPert (1730 diffractometer). The latter appears with Cu Kα (α = 1.54056 A°) and voltage of 40 kV. Surface area and isotherm are tested by N_2 adsorption–desorption (Micrometritics, TriStar II 3020 surface area and porosity analyzer). The particle morphology is examined by scanning electron microscopy (SEM) [(HITACHI S-4160)], on gold coated samples. Shimadzu-UV-2550-8030 spectrophotometer is used for analysis of the UV-Vis diffuse reflectance spectroscopy (DRS) in the range of 190-800 nm.

2.2. Preparation of the catalyst

The Ni/Cu-MCM-41 is prepared through co-condensation method [41]. According to this procedure, about 0.65 g of cetyltrimethylammonium bromide (CTAB) is dissolved in 50 mL of H_2O and ethanol. Afterwards, 4 mL of an aqueous NH_3 solution containing 0.102 g of $Cu(NO_3)_2$. $3H_2O$ and 0.5 g of $Ni(NO_3)_2$. $6H_2O$ is added to formation a dark blue color solution. Subsequently, about 3.2 mL of tetraethyl orthosilicate (TEOS) is added and stirred for 2 h at room temperature (RT). This procedure is followed by filtering blue color product, washing it with deionized water, drying at 75°C overnight, and calcination at 540°C, for 18 h.

2.3. General procedure for the Sonogashira coupling reaction in the presence of the Ni/Cu-MCM-41

A mixture of phenylacetylene (1.2 mmol), aryl halide (1 mmol), KOH (2 mmol), DMF (5 mL) and Ni/Cu-MCM-41 (20 mg) are added into a 25 mL flask. The resulting mixture is stirred at 120 °C for appropriate reaction time. Progress of reactions is monitored by TLC. After completion of the reaction, the catalyst is separated by centrifugation. Then, the reaction mixture is extracted with ethyl acetate and water. The organic phase is dried by addition of $MgSO_4$ and concentrated under reduced pressure. The residue is purified by column chromatography.

3. Results and discussion

3.1. Characterization of the catalyst

Upon synthesis, Ni/Cu-MCM-41 is characterized by FT-IR, SEM, XRD, DRS, energy dispersive X-ray spectroscopy (EDX), and nitrogen adsorption–desorption analysis.

FT-IR spectra of MCM-41 (Mobil Composition of Matter No. 41) and Ni/Cu-MCM-41 are recorded in the range of 400–4000 cm^{-1} (Fig. S1 of the SI). In both spectra, the broad band at around 3430 cm^{-1} is correlated to the hydroxyl stretching vibrations of the silanols and adsorbed water molecules, also the H–O–H bending vibration of water molecules is assigned at around 1635 cm^{-1}. For MCM-41, the band at 1088 cm^{-1} can be assigned to asymmetric Si–O–Si stretching vibration. It can be seen in FT-IR spectra of Ni/Cu-MCM-41 that this band is shifted to the lower wave number at 1083 cm^{-1}, because substitution of Si atoms with Cu and Ni causes the longer bond lengths of Cu–O and Ni–O bonds in comparison with Si–O bonds. In addition, Si–O–Si bending vibration is observed at 459 cm^{-1}. These results demonstrate the successful incorporation of transition metals in the framework of MCM-41.

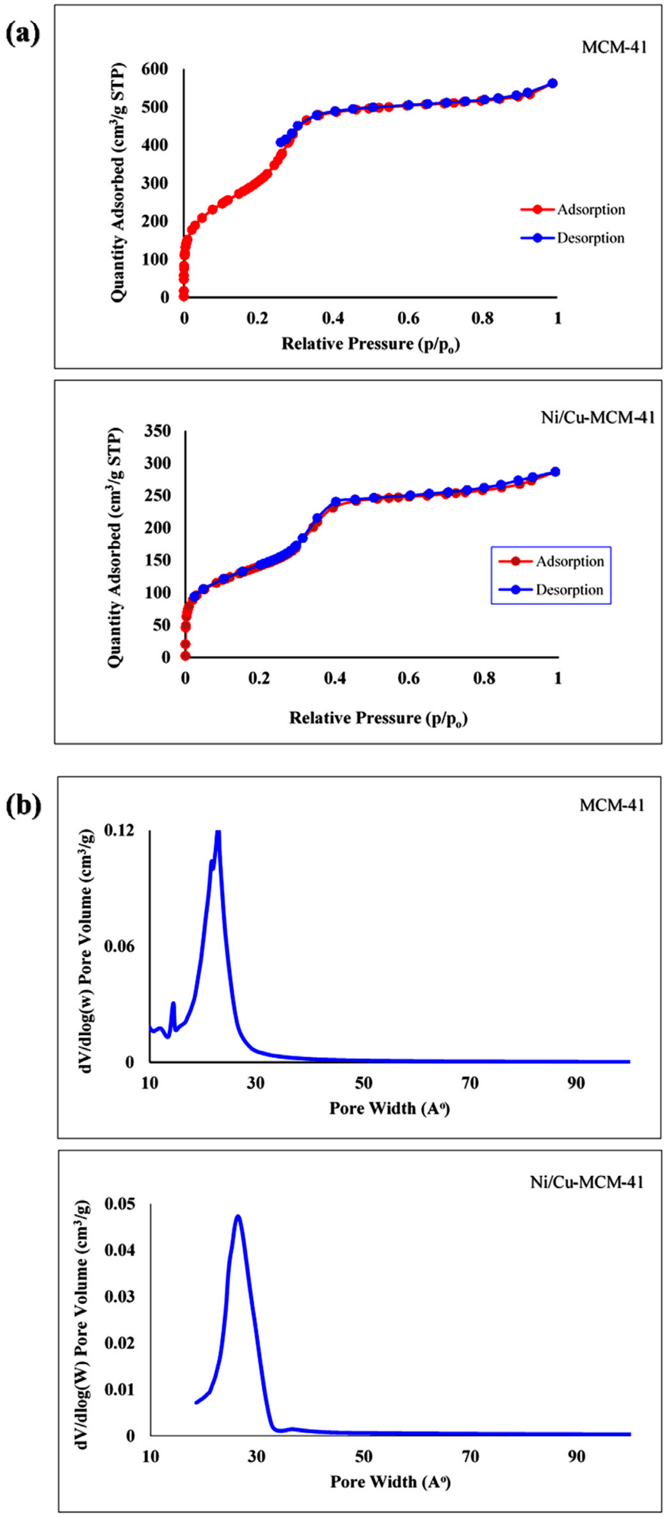


Fig. 1. Nitrogen adsorption–desorption isotherms (a) and pore size distribution (b) of MCM-41 and Ni/Cu-MCM-41.

The crystal structure of sample is characterized by XRD measurement (Fig. S2 of the SI). The low angle XRD pattern of Ni/Cu-MCM-41 exhibits a strong peak in 2θ =1.24, due to the d_{100} plane, which is the characteristic diffraction pattern of the ordered hexagonal symmetry of mesoporous material. Comparison of XRD pattern of Ni/Cu-MCM-41 with MCM-41 indicates a decrease in 2θ

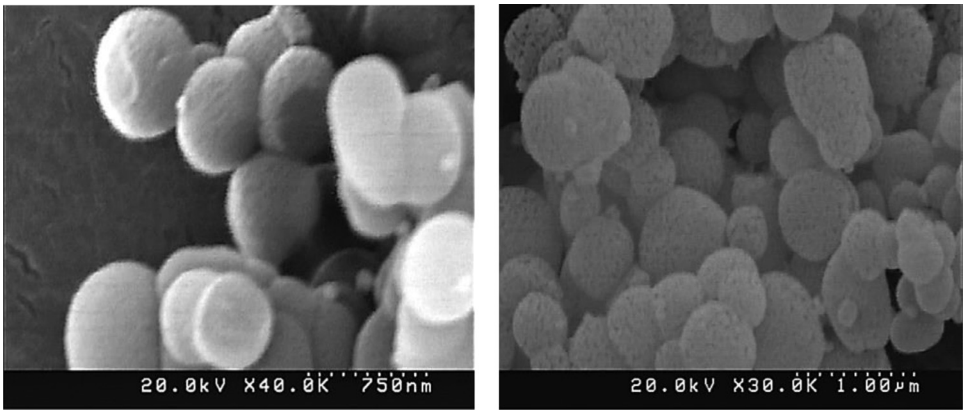


Fig. 2. SEM images of the Ni/Cu-MCM-41.

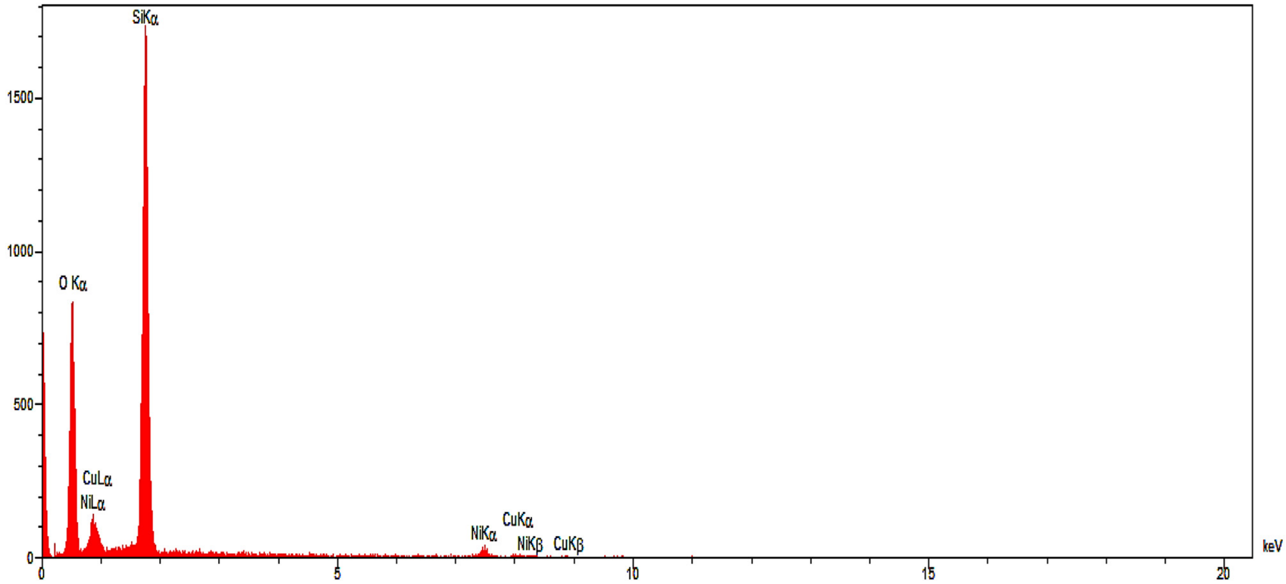


Fig. 3. The EDX spectrum of the Ni/Cu-MCM-41.

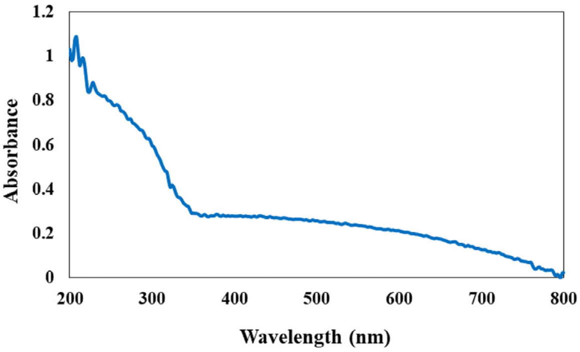


Fig. 4. The UV-Vis diffused reflectance spectra (DRS) of Ni/Cu-MCM-41.

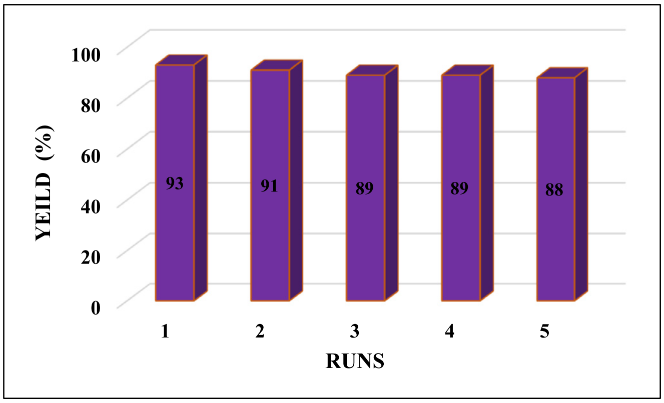
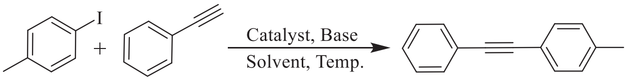


Fig. 5. Reusability study of the catalyst in the Sonogashira cross-coupling reaction.

value of the (100) reflection, which is probably due to the ionic radii of Ni^{2+} and Cu^{2+} that are larger than that of Si^{4+}. So, the partial substitution of the structural Si^{4+} by these metals has resulted in an increase in the d spacing and decrease in the 2θ based on the Bragg's equation. The wide angle XRD pattern of Ni/Cu-MCM-41 shows the broad peak at around 22.5°, corresponding to the amorphous silica. Slight extent of NiO with cubic phase confirms good dispersion of copper and nickel ions in the MCM-41 framework (Fig. S2c).

The nitrogen adsorption–desorption isotherms of MCM-41 and Ni/Cu-MCM-41 reveal an type IV adsorption isotherm with a capillary condensation step at a low relative pressure (P/P_0= 0.2–0.4), confirming the characteristics of a mesoporous structure. This sharp inflection move slightly to higher relative pressure with

Table 1
Screening of reaction parameters for the Sonogashira coupling reaction catalyzed by Ni/Cu-MCM-41.[a]



Entry	Solvent	Catalyst Amount (mg)	Base	Temperature (°C)	Yield[b] (%)
1	DMF	20	K_2CO_3	120	50
2	DMF	20	Na_2CO_3	120	40
3	DMF	20	NaOH	120	60
4	DMF	20	Et_3N	120	30
5	DMF	20	KOH	120	93
6	EtOH	20	KOH	120	65
7	H_2O	20	KOH	120	10
8	DMSO	20	KOH	120	60
9	Toluene	20	KOH	120	50
10	DMF	15	KOH	120	80
11	DMF	10	KOH	120	70
12	DMF	20	KOH	80	50
13	DMF	20	KOH	100	60
14	DMF	20	KOH	140	94

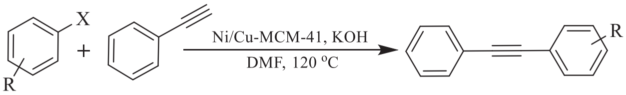
[a] Reaction conditions: phenylacetylene (1.2 mmol), 4-iodotoluene (1.0 mmol), base (2 mmol), solvent (5 mL).
[b] Isolated yield.

transition-metal incorporation. The Brunauer- Emmett-Teller (BET) surface and pore volume of MCM-41 are calculated to be 927 m^2/g and 0.86 cm^3/g, respectively. While, the BET surface (469 m^2/g) and pore volume (0.44 cm^3/g) for Ni/Cu-MCM-41 are lower than those for MCM-41(Fig. 1a). According to the Barrett-Joyner-Halenda (BJH) model, pore size distribution of MCM-41 and Ni/Cu-MCM-41 are 2.2 and 2.6 nm, respectively (Fig. 1b).

In order to have a vision on surface topography and the morphological dispersion of the metal particles over mesoporous substrate, SEM analysis has been performed for MCM-41 modified with Cu and Ni. The images indicate that the particles are spherical in nature and the metal particles are well dispersed over the surface of mesoporous support (Fig. 2). The EDX spectrum also confirms the elemental distribution of Ni/Cu-MCM-41 including O, Si, Ni and Cu (Fig. 3).

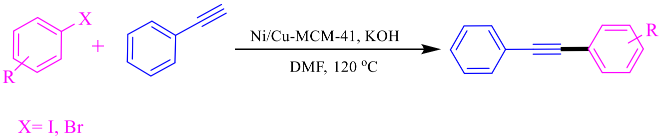
The coordination environment of the copper and nickel modified MCM-41 is investigated by UV–Visible analysis. A highly intense peak below 300 nm in the (DR) spectra of Ni/Cu-MCM-41 may be attributed to the ligand to metal (Cu and Ni) charge transfer transition. The band around 780 nm, corresponds to the $^2E_g(D)$-$^2T_{2g}$ spin and allows Lapporte-forbidden transition of Cu^{2+} in the octahedral coordination [41] (Fig. 4).

Table 2
Sonogashira couplings of various aryl halides and phenylacetylene over Ni/Cu-MCM-41.



Entry	R	X	Time (h)	Yield[a] (%)
1	H	I	6	95
2	4-CH_3	I	6	93
3	4-OCH_3	I	8	90
4	3-OCH_3	I	8	87
5	3-NH_2	I	8	85
6	2-NH_2	I	8	84
7	1-Cl	I	6	90
8	4-NO_2	I	5	96
9	4-Br	I	8	80
10	H	Br	6	82
11	4-COH	Br	8	78
12	3-COH	Br	8	65

[a] Isolated yield.

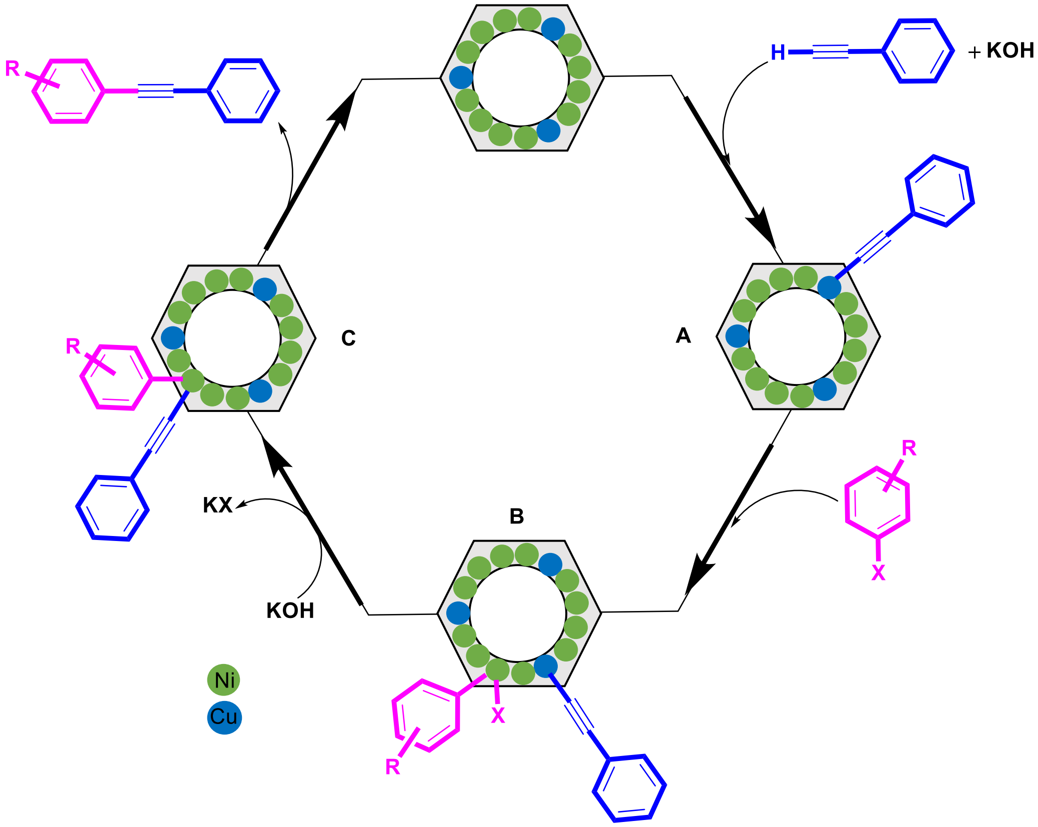


Scheme 1. Sonogashira cross-coupling reaction by Ni/Cu-MCM-41.

3.2. Catalytic activity studies

After the detailed characterization of Ni/Cu-MCM-41, its catalyst activity is assessed in the Sonogashira coupling reaction. Initially, the Ni/Cu-MCM-41 catalyzed Sonogashira reaction conditions are optimized by screening various solvents, catalyst amounts, basic compounds, and temperatures in the coupling reaction of 4-iodotoluene and phenylacetylene (Table 1). Bases play a major role in coupling reactions, testing various bases (KOH, NaOH, K_2CO_3, Na_2CO_3 and Et_3N) show that the best yield is obtained by using KOH (Table 1, entries 1–5). Next, a variety of solvents (DMF, DMSO, EtOH, H_2O and toluene) are probed for the model reaction, where DMF affords the highest yield (Table 1, entries 5–9). Testing different amounts of the catalyst (10, 15 and 20 mg), 20 mg of Ni/Cu-MCM-41 is found to be the optimum amount (Table 1, entries 5, 10, 11). Finally, efficiency of the several temperatures (80, 100, 120 and 140 °C) is tested in Sonogashira reaction, where 120 °C shows the best performance. It should be noted that the increase of temperature does not affect the product yield (Table 1, entries 12–14). Based on results, the optimum reaction conditions for Ni/Cu-MCM-41 catalyzed Sonogashira reactions are found to be KOH as the base, DMF as the solvent, 20 mg of Ni/Cu-MCM-41 as the amount catalyst, and 120 °C as the optimum temperature.

Using the above optimized reaction conditions, the scope of the Sonogashira couplings is examined for the synthesis of diverse alkyne-functionalized benzenes using a broad of aryl halides. The results indicate that the Sonogashira reaction proceeds efficiently with both aryl iodides and aryl bromides affording C-C coupling products in good yields (Table 2). The aryl iodides bearing electron-donating groups (-CH_3 and -OCH_3) at *para*-substituted position afford cross-coupling products with excellent yields (Table 2, entries 2, 3). However, the aryl iodides with *meta-* or *ortho*-substituted electron-donating groups provide the coupled product in slightly lower yields (Table 2, entries 4-6). Aryl iodide with electron-withdrawing groups (-Cl, -Br and -NO_2) are successfully coupled to biphenylacetylene derivatives in good yields (Table 2,



Scheme 2. Proposed mechanism for the Ni/Cu-MCM-41 catalyzed Sonogashira cross-coupling reaction.

entries 7-9). On the other hand, the Ni/Cu-MCM-41 catalyzed Sonogashira couplings is investigated also for the aryl bromides that show the bromo-substituted substrates are more difficult than those of corresponding iodo-substituted aromatics (Table 2, entries 10-12).

A plausible mechanism for the Ni/Cu-MCM-41 catalyzed Sonogashira cross-coupling reaction has been presented in Scheme 2. At first, catalyst activates phenylacetylene to form Cu-acetylide intermediate (A) in the presence of base. Subsequently, aryl halide is adsorbed on the Ni/Cu-MCM-41 surface through oxidative addition to form ArNiX species (B). Next, in the transmetalation step, the halide is readily displaced with terminal alkyne to form intermediate C. Finally, the dipheylacetylene product is formed from the resulting intermediate C by reductive elimination.

3.3. Recycling of the catalyst

The reusability of heterogeneous catalyst is a key aspect to evaluate its efficiency that is a crucial factor from eco-friendly and economical points of view. In this regard, we carry out the reusability of Ni/Cu-MCM-41 catalyst in the Sonogashira coupling reaction of 4-iodotoluene and phenylacetylene under the optimized conditions (Fig. 5). After completion of the reaction, the catalyst easily is separated by centrifugation from the reaction solution, washed with acetone, dried and reused in the next run. It is noteworthy that the catalyst could be used five times without a significant loss in its activity.

4. Conclusions

We have successfully used Ni/Cu-MCM-41 as a convenient catalyst in Sonogashira coupling of different aryl halides with phenylacetylene under palladium-free conditions. It is found, that the present bimetallic mesoporous system is one of the most effective catalysts for the synthesis of various diphenylacetylenes and could be successfully recovered from the reaction mixture and reused for five consecutive catalytic cycles without significant loss of its activity. Moreover, this protocol is prominent because of the use of low cost catalytic system respect to palladium catalyst and open new perspectives for the application of bimetallic catalysts in coupling reactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121703.

References

[1] M. Lamblin, L. Nassar-Hardy, J. Hierso, E. Fouquet, F. Felpin, Recyclable heterogeneous palladium catalysts in pure water: sustainable developments in Suzuki, Heck, Sonogashira and Tsuji–Trost reactions, Adv. Synth. Catal. 352 (2010) 33–79.

[2] R. Ciriminna, V. Pandarus, G. Gingras, F. Béland, P. Demma Carà, M. Pagliaro, Heterogeneous Sonogashira coupling over nanostructured Silia Cat Pd (0), ACS Sustain. Chem. Eng. 1 (2013) 57–61.

[3] A. Sagadevan, K.C. Hwang, Photo-induced Sonogashira C□ C coupling reaction catalyzed by simple copper (I) chloride salt at room temperature, Adv. Synth. Catal. 354 (2012) 3421–3427.

[4] A.R. Hajipour, F. Rezaei, Z. Khorsandi, Pd/Cu-free Heck and Sonogashira cross–coupling reaction by Co nanoparticles immobilized on magnetic chitosan as reusable catalyst, Green Chem 19 (2017) 1353–1361.

[5] K. Sonogashira, Y. Tohda, N. Hagihara, A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines, Tetrahedron Lett. 16 (1975) 4467–4470.

[6] J. Tan, Y. Bai, X. Zhang, C. Huang, D. Liu, L. Zhang, Low-temperature synthesis of thermoresponsive diblock copolymer nano-objects via aqueous photoinitiated polymerization-induced self-assembly (photo-PISA) using thermoresponsive macro-RAFT agents, Macromol. Rapid Commun. 37 (2016) 1434–1440.

[7] C. Jung, M. Krumova, S. Mecking, Hybrid nanoparticles by step-growth Sonogashira coupling in disperse systems, Langmuir 30 (2014) 9905–9910.

[8] F.F. Wagner, D.L. Comins, Expedient five-step synthesis of SIB-1508Y from natural nicotine, J. Org. Chem. 71 (2006) 8673–8675.

[9] K.C. Nicolaou, W. Dai, Chemistry and biology of the enediyne anticancer antibiotics, Angew. Chem. Int. Ed. Engl. 30 (1991) 1387–1416.

[10] N. Matsumi, K. Naka, Y. Chujo, Extension of π-conjugation length via the vacant p-orbital of the boron atom. Synthesis of novel electron deficient π-conjugated systems by hydroboration polymerization and their blue light emission, J. Am. Chem. Soc. 120 (1998) 5112–5113.

[11] R.E. Martin, F. Diederich, Linear monodisperse π-conjugated oligomers: model compounds for polymers and more, Angew. Chem. Int. Ed. 38 (1999) 1350–1377.

[12] M. Inouye, K. Takahashi, H. Nakazumi, Remarkably strong, uncharged hydrogen-bonding interactions of polypyridine-macrocyclic receptors for deoxyribofuranosides, J. Am. Chem. Soc. 121 (1999) 341–345.

[13] S.H. Chanteau, J.M. Tour, Synthesis of potential molecular electronic devices containing pyridine units, Tetrahedron Lett. 42 (2001) 3057–3060.

[14] Z. Novák, A. Szabó, J. Répási, A. Kotschy, Sonogashira coupling of aryl halides catalyzed by palladium on charcoal, J. Org. Chem. 68 (2003) 3327–3329.

[15] C.C.C. Johansson Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, Palladium–catalyzed cross-coupling: a historical contextual perspective to the 2010 Nobel Prize, Angew. Chem. Int. Ed. 51 (2012) 5062–5085.

[16] L. Anastasia, E. Negishi, Highly satisfactory procedures for the Pd-catalyzed cross coupling of aryl electrophiles with in situ generated alkynylzinc derivatives, Org. Lett. 3 (2001) 3111–3113.

[17] R. Chinchilla, C. Nájera, Recent advances in Sonogashira reactions, Chem. Soc. Rev. 40 (2011) 5084–5121.

[18] F.M. Moghaddam, G. Tavakoli, H.R. Rezvani, A copper-free Sonogashira reaction using nickel ferrite as catalyst in water, Catal. Commun. 60 (2015) 82–87.

[19] M.B. Thathagar, J. Beckers, G. Rothenberg, Palladium-free and ligand-free Sonogashira cross-coupling, Green Chem. 6 (2004) 215–218.

[20] B. Wang, Y. Wang, X. Guo, Z. Jiao, G. Jin, X. Guo, Reduced graphene oxide supported Cu$_2$O nanoparticles as an efficient catalyst for Sonogashira coupling reaction, Catal. Commun. 101 (2017) 36–39.

[21] H. Zhao, B. Huang, Y. Wu, M. Cai, MCM-41-immobilized Schiff base-pyridine bidentate copper (I) complex as a highly efficient and recyclable catalyst for the Sonogashira reaction, J. Organomet. Chem. 797 (2015) 21–28.

[22] A.A. Liori, I.K. Stamatopoulos, A.T. Papastavrou, A. Pinaka, G.C. Vougioukalakis, A Sustainable, User-friendly protocol for the Pd-free Sonogashira coupling reaction, Eur. J. Org. Chem. 2018 (2018) 6134–6139.

[23] F. Monnier, F. Turtaut, L. Duroure, M. Taillefer, Copper-catalyzed Sonogashira–type reactions under mild palladium-free conditions, Org. Lett. 10 (2008) 3203–3206.

[24] Z. Wang, T. Zheng, H. Sun, X. Li, O. Fuhr, D. Fenske, Sonogashira reactions of alkyl halides catalyzed by NHC [CNN] pincer nickel (II) complexes, New J. Chem. 42 (2018) 11465–11470.

[25] J. Yin, W. Chai, F. Zhang, H. Li, Periodic mesoporous silica-supported Ni (II) organometallic complex as an active and reusable nanocatalyst for water-medium Sonogashira coupling reaction, Appl. Organomet. Chem. 27 (2013) 512–518.

[26] L. Wang, P. Li, Y. Zhang, The Sonogashira coupling reaction catalyzed by ultrafine nickel (0) powder, Chem. Commun. (2004) 514–515.

[27] J. Santandrea, A.-C. Bédard, S.K. Collins, Cu (I)-catalyzed macrocyclic Sonogashira-type cross-coupling, Org. Lett. 16 (2014) 3892–3895.

[28] D. Ma, F. Liu, CuI-catalyzed coupling reaction of aryl halides with terminal alkynes in the absence of palladium and phosphine, Chem. Commun. (2004) 1934–1935.

[29] M.A. Bhosale, T. Sasaki, B.M. Bhanage, A facile and rapid route for the synthesis of Cu/Cu$_2$O nanoparticles and their application in the Sonogashira coupling reaction of acyl chlorides with terminal alkynes, Catal. Sci. Technol. 4 (2014) 4274–4280.

[30] E. Niknam, A. Moaddeli, A. Khalafi-Nezhad, Palladium anchored on guanidine-terminated magnetic dendrimer (G3-Gu-Pd): an efficient nano-sized catalyst for phosphorous-free Mizoroki-Heck and copper-free Sonogashira couplings in water, J. Organomet. Chem. 923 (2020) 121369.

[31] B. Jin, F. Gallou, J. Reilly, B.H. Lipshutz, ppm Pd-Catalyzed, Cu-free Sonogashira couplings in water using commercially available catalyst precursors, Chem. Sci. 10 (2019) 3481–3485.

[32] S. Handa, J.D. Smith, Y. Zhang, B.S. Takale, F. Gallou, B.H. Lipshutz, Sustainable HandaPhos-ppm palladium technology for copper-free Sonogashira couplings in water under mild conditions, Org. Lett. 20 (2018) 542–545.

[33] S. Handa, B. Jin, P.P. Bora, Y. Wang, X. Zhang, F. Gallou, J. Reilly, B.H. Lipshutz, Sonogashira couplings catalyzed by fe nanoparticles containing ppm levels of reusable Pd, under mild aqueous micellar conditions, ACS Catal. 9 (2019) 2423–2431.

[34] M. Sankar, N. Dimitratos, P.J. Miedziak, P.P. Wells, C.J. Kiely, G.J. Hutchings, Designing bimetallic catalysts for a green and sustainable future, Chem. Soc. Rev. 41 (2012) 8099–8139.

[35] R.K. Rai, D. Tyagi, K. Gupta, S.K. Singh, Activated nanostructured bimetallic catalysts for C–C coupling reactions: recent progress, Catal. Sci. Technol. 6 (2016) 3341–3361.

[36] D.R. Pye, N.P. Mankad, Bimetallic catalysis for C–C and C–X coupling reactions, Chem. Sci. 8 (2017) 1705–1718.

[37] D.N. Olekszyszen, B.L. Albuquerque, D. de O. Silva, G.L. Tripodi, D.C. de Oliveira, J.B. Domingos, Core-shell PdCu bimetallic colloidal nanoparticles in Sonogashira cross-coupling reaction: mechanistic insights into the catalyst mode of action, Nanoscale 12 (2020) 1171–1179.

[38] A. Abolhosseini Shahrnoy, A.R. Mahjoub, S. Shokrollahi, N. Ezzati, K. Elsner, C.T. Koch, Step-by-step synthesis of copper (I) complex supported on platinum nanoparticle-decorated mesoporous silica hollow spheres and its remarkable catalytic performance in Sonogashira coupling reaction, Appl. Organomet. Chem. 34 (2020) e5645.

[39] W. Chang, J. Shin, G. Chae, S.R. Jang, B.J. Ahn, Microwave-assisted Sonogashira cross-coupling reaction catalyzed by Pd-MCM-41 under solvent-free conditions, J. Ind. Eng. Chem. 19 (2013) 739–743.

[40] S.M. Sarkar, M.M. Yusoff, M.L. Rahman, Mesoporous silica MCM-41 supported n-heterocyclic carbene-Pd complex for Heck and Sonogashira coupling reactions, J. Chinese Chem. Soc. 62 (2015) 33–40.

[41] D. Rath, K.M. Parida, Copper and nickel modified MCM-41 an efficient catalyst for hydrodehalogenation of chlorobenzene at room temperature, Ind. Eng. Chem. Res. 50 (2011) 2839–2849.