



Entangled nanofibrous copper: an efficient and high performance nanostructured catalyst in azide-alkyne cycloaddition reaction and reduction of nitroarenes and aromatic aldehydes

Seyyed Jafar Saghanezhad¹ · Maryam Mozafari Buhamidi² · Soghra Ebadi² · Narges Taheri² · Soheil Sayyahi² 

Received: 22 March 2021 / Accepted: 16 June 2021 / Published online: 23 June 2021
© Akadémiai Kiadó, Budapest, Hungary 2021

Abstract

In this research, nanofibrous copper (0) was utilized as an efficient nanostructured catalyst in Azide-Alkyne Cycloaddition reaction, reduction of nitrobenzenes to anilines and reduction of aromatic aldehydes to benzyl alcohols. Nanofibrous copper was prepared via dealloying of Cu–Zn powder and was characterized by SEM, TEM, XRD, BET and EDS analyses. This catalyst produced very good results including high product yield, short reaction time and recyclability.

Keywords Nanofibrous copper · 1,2,3-triazole derivatives · Reduction of nitroarenes · Reduction of carbonyl

Introduction

In recent decades, preparation of porous materials has been a very interesting research field [1]. Apart from zeolites which have natural counterparts [2], metal–organic frameworks [3], porous silicas such as SBA-15 [4] and MCM-41 [5], and covalent organic frameworks [6] have been the subjects of extensive research. A wide variety of methods have been developed for preparing porous metals, including the template method, magnetron sputtering, electrodeposition, and the dealloying process [7]. Porous metals have been used in electrochemical sensors, electrochemical energy systems [8], as well as for electrochemical catalysis and surface-enhanced Raman scattering (SERS) [9].

✉ Soheil Sayyahi
sayyahi.soheil@gmail.com

¹ ACECR-Production Technology Research Institute, Ahvaz, Iran

² Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

Dealloying is a very reliable method for preparing porous metals such as gold, in which Ag–Au alloys immersed in nitric acid are dealloyed under free corrosion conditions [10]. The sequential elemental dealloying approach has also been used for the fabrication of porous metal oxides, whose sensors have been exploited for electronic listening [11]. Copper dealloying has also been applied with binary alloys like Mn–Cu [12], Cu–Zr [13], Mg–Cu [14], Al–Cu [15], Ti–Cu [16], and also ternary alloys such as Al–Cu–Mg [17], Ti–Cu–Ag [18] to prepare porous copper. The porosity is dependent on such conditions as potentiostatic dealloying and free corrosion.

N-substituted 1,2,3-triazoles have been prepared through click synthesis in the presence of a Cu (I) catalyst [19]. In addition, a microwave-assisted click chemistry synthesis of 1,4-disubstituted 1,2,3-triazoles via a copper (I)-catalyzed three-component reaction [20] as well as, a synthesis of 1,4-disubstituted 1,2,3-triazoles from in situ generated azides [21], as well as a regioselective synthesis of 1,4,5-trisubstituted 1,2,3-triazoles via copper-catalyzed azide–alkyne cycloaddition has been reported [22]. Furthermore, multicomponent click synthesis of 1,2,3-triazoles from epoxides has been demonstrated to be catalyzed by copper nanoparticles on activated carbon [23]. Selective catalytic reduction of nitro compounds into their amine counterparts is of great value in organic synthesis [24]. The reduction of (i) p-nitrophenol and (ii) hexacyanoferrate (III) by borohydride ions is used as catalytic model reactions for evaluating the catalytic activity of nanocatalysts. It is worth noting that, no reaction should take place in the absence of nanoparticles [25]. Several catalysts have been utilized for this transformation including Raney nickel [26], molybdenum hexacarbonyl and DBU under microwave irradiation [27], carbon monoxide and water in the presence of the PdCl₂/Fe/I₂ system [28], surface modification of TiO₂ nanoparticles [29], zeolite-supported copper nanoparticles with 2-propanol as a sustainable reducing agent [30], graphene–ZnO–Au nanocomposites [31], magnetic core–shell nanocatalyst [32], palladium supported on magnetic nanoparticles modified with carbon quantum dots [33], COF-Supported Co/Co(OH)₂ nanoparticles [34], hydrazine–Fe₃O₄ [35], Fe₃O₄@sepiolite–Pd²⁺ [36], and supported gold nanoparticles [37]. Furthermore, the reduction of carbonyl compounds to the corresponding alcohols is considered an important transformation in the synthesis of biologically active compounds [38], with several catalysts such as Ni nanoparticles [39], zeolite supported Cu nanoparticles [40], Raney Ni–Al alloy and Al powder [41] and ball milling with NaBH₄ [42] having been proposed for this purpose. Given the importance of these transformations in organic synthesis, there is a need for easier, simpler and more efficient methods that overcome the disadvantages. Considering the great versatility of porous and nano-sized copper [43], we decided to utilize the synergic effect of its high surface area and its splendid activity in the catalysis of organic reactions including azide–alkyne cycloaddition reaction, reduction of nitrobenzenes to anilines, and reduction of aromatic aldehydes to benzyl alcohols [44].

Results and discussion

In the first step, nanofibrous copper (0) was prepared via controlled etching of Cu–Zn alloy by NaOH solution. The etching creates porous sites in the metal texture, accessible by the reactants, and increases the surface area; thus, increasing the

reaction rate by providing a greater catalyst- reactant interface. Terminal atoms of interfaces in heterogeneous catalysts have been demonstrated to have higher energy, resulting in a stronger interaction between the catalyst surface and reactant molecules [45]. To verify the structure of the nanocatalyst, several characterization techniques were used including SEM, TEM, XRD, BET and EDS analyses. The SEM images of the nanofibrous copper and the Cu–Zn alloy were recorded to allow a comparison of the surface structure of the metal to be made (Fig. 1). The Cu metal has a very smooth and solid texture before etching. After dealloying of Cu–Zn alloy, the Cu nanofibrous framework stays and the Zn is etched. Accordingly, the porous structure is formed, which is apparent in SEM images. Comparing the Cu–Zn alloy and nanostructured Cu, the difference in the surface texture can be easily detected. It can be seen that nanostructured Cu has a porous structure resembling that of a woven fabric, and can provide ample space for the starting materials to accumulate. The porous nature of the copper catalyst was also examined through transmission electron microscopy (TEM). As can be vividly seen in the TEM image, the metal particles are very transparent, indicating their porous nature (Fig. 2).

The BET test was also conducted to evaluate the gas adsorption capacity of the porous catalyst (Fig. 3). According to the BET analysis, the surface area was calculated to be $8.9 \text{ m}^2/\text{g}$. It can be concluded from the BET and SEM analyses that the copper texture changed into a fibrous structure form, which can prove more

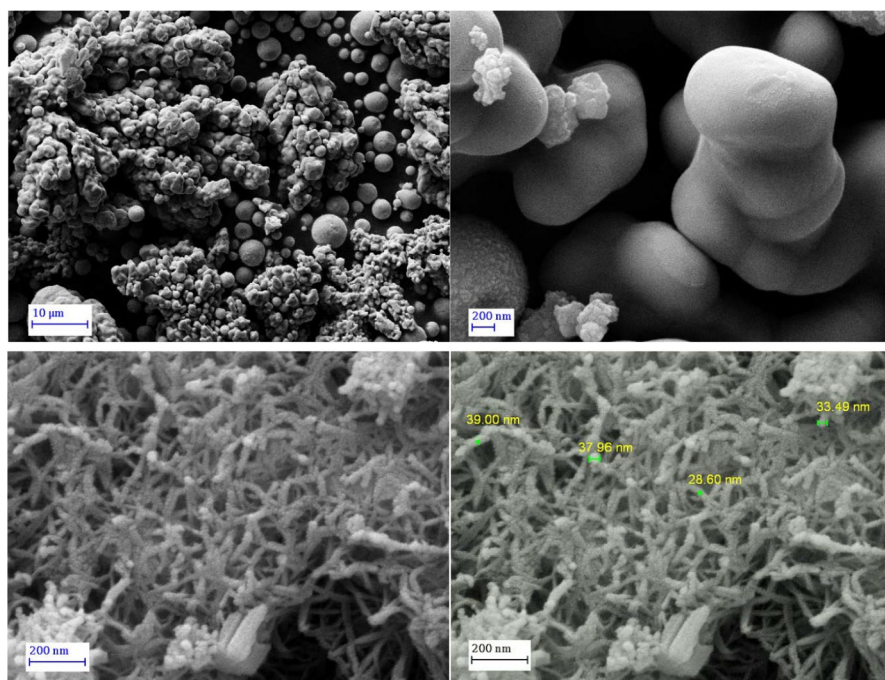


Fig. 1 The SEM images of Cu–Zn alloy before etching (upper; Zn=92.3 wt%, Cu=7.7 wt%) and the structure of nanofibrous copper (0) (lower; Zn=8.8 wt%, Cu=91.2 wt%)

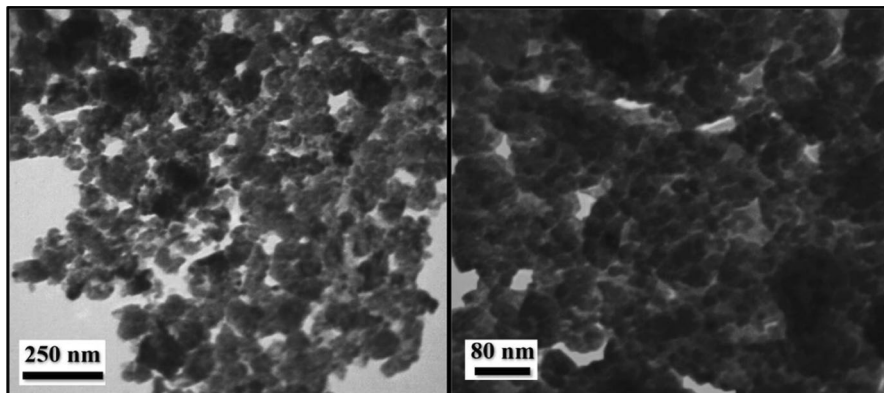


Fig. 2 The TEM images of nanofibrous copper (0)

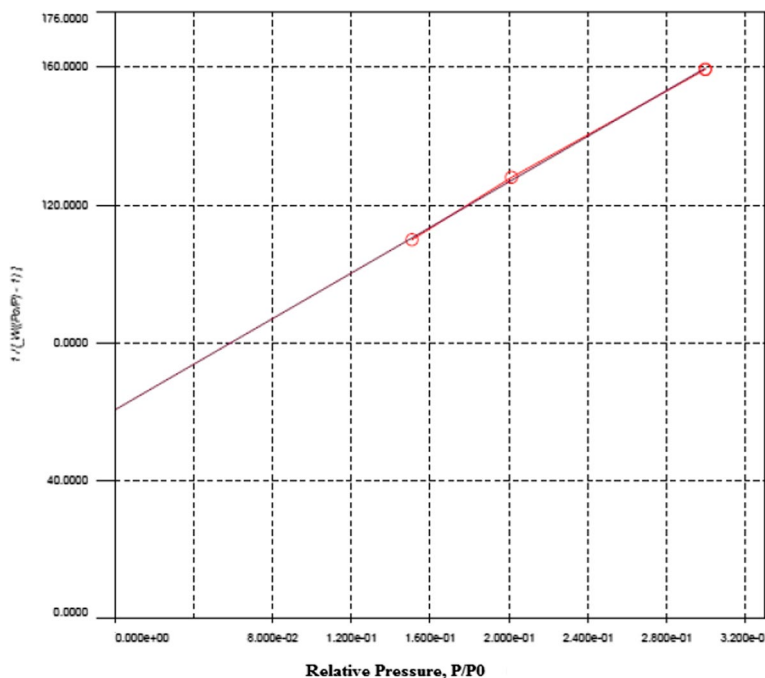


Fig. 3 BET analysis of nanofibrous Cu (0)

beneficial in providing a greater surface area than solid metal as the catalyst in the chemical reactions.

In the next step, the XRD pattern of the nanoporous copper was recorded (Fig. 4). According to the Debye-Scherrer equation, the crystallite size was calculated to be 98.7 nm for the peak at $2\theta = 43.4^\circ$.

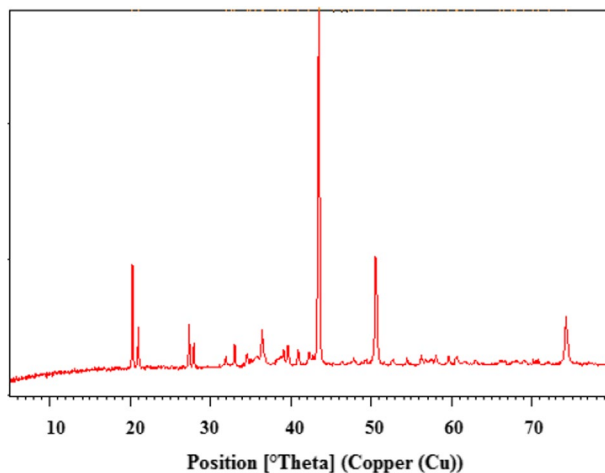


Fig. 4 The XRD pattern of nanofibrous copper (0)

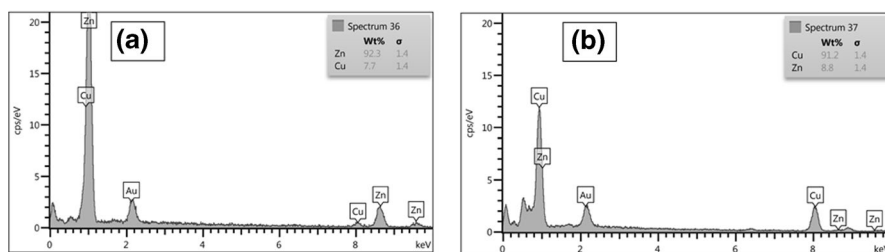
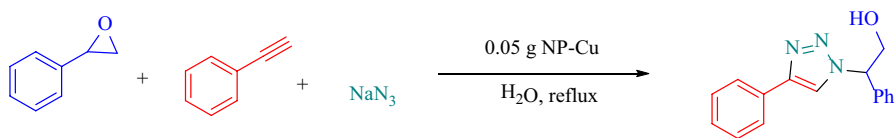


Fig. 5 The EDS analysis of **a** Cu–Zn alloy, and **b** Nanofibrous copper (after dealloying)

It should also be pointed out that the dealloyed content was considerable according to the EDS analysis (Fig. 5). Before dealloying the Cu–Zn alloy had 92.3% of Zn content compared to 8.8% after dealloying.

After the characterization of the nanofibrous copper, it was decided to utilize this catalyst in the one-pot preparation of 1,2,3-triazole derivatives via azide-alkyne cycloaddition reaction. The reaction was conducted with a mixture of phenyl acetylene (1 mmol), sodium azide (1 mmol), epoxide/alkyl chloride (1 mmol), nano-porous copper (0.05 g) and distilled water (5 mL) under reflux conditions (Scheme 1). The reaction was found to be completed after 6 h, and the corresponding product namely 2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl) ethan-1-ol was isolated.

Delighted with this result, we decided to prepare the similar products using the same method. As a result, a series of the 1,2,3-triazole derivatives were prepared (Table 1). According to the results, it was found out that the sole product in the ring opening of the epoxides, is the product which was prepared by the nucleophilic attack to the less hindered position of the epoxide ring except for styrene oxide.



Scheme 1 Model reaction for the one-pot preparation of 1,2,3-triazole derivatives. Conditions: 80 °C, 6 h

After the satisfactory results obtained from the synthesis of 1,2,3-triazole derivatives, we tried to broaden the scope of catalytic activity of the catalyst; thus the reduction reactions were selected as model reactions. In reduction reactions, metal catalysts are utilized to enhance the reaction rate. Metals facilitate the electron and hydrogen transfer on their surface. Given the greater surface area provided by the nanofibrous Cu, it was considered a logical choice for selection as a good catalyst in this reaction. Accordingly, the reduction of nitrobenzenes to anilines was chosen as a benchmark. As a model reaction, nitrobenzene (1 mmol), sodium borohydride (2 mmol), nano-porous copper (0.01 g) and ethanol (5 mL) were heated at reflux conditions. Surprisingly, after 30 min, the reaction was complete and aniline was obtained. It should be noted that the reaction produced negligible yields after 2 h in the absence of the catalyst. Afterwards, a series of nitrobenzenes were converted into their corresponding aniline derivatives (Table 2).

In a similar vein, nanofibrous Cu was used to prepare benzyl alcohols from aromatic aldehyde derivatives (Table 3). Easy post-reaction recovery separation and catalyst reusability are among the great advantages of heterogeneous catalysts. In this regard, after completion of nitrobenzene reduction reaction, the catalyst was removed by simple filtration, washed with ethanol (5 mL) and then reused seven times without significant loss of activity (Fig. 6).

To assess the stability of the catalyst [47], The conversion versus the reaction time was plotted for the nitrobenzene reduction reaction in the presence of the catalyst. It was obvious that the deactivation of the catalyst occurs in the following runs due to the change in the apparent rate constant in the consecutive experimental runs (Fig. 7).

To demonstrate the superiority of the catalytic performance of nanofibrous copper over the reported catalysts, the reduction of nitrobenzene to aniline was regarded as a representative example (Table 4). While in the majority of cases (except for entry 4), comparative yields of the desired product were obtained following the nanofibrous copper-catalyzed procedure, the reported procedures required long reaction time periods (entry 1), or high catalyst loading (entries 1–4). These results clearly demonstrate that nanofibrous copper is an equally or more efficient catalyst for this reaction.

Table 1 One-pot preparation of 1,2,3-triazole derivatives

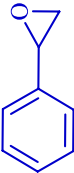
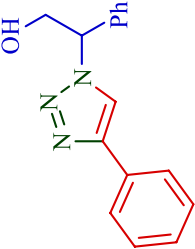

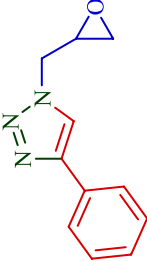

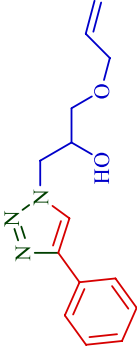
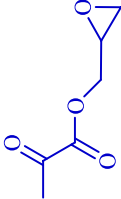
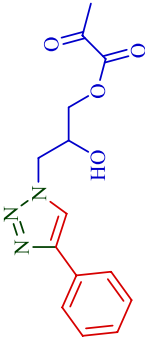
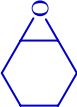
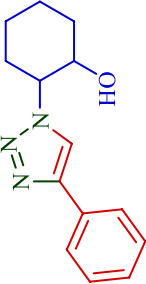

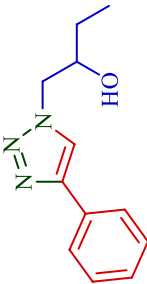
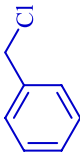
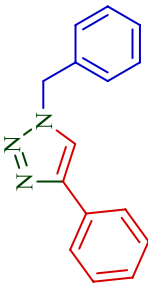

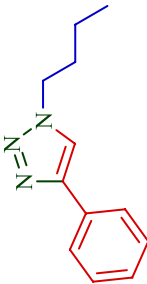
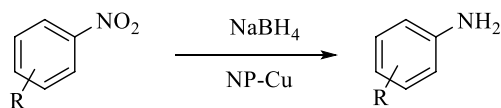
Entry	Epoxide	Product	Yield ^a (%)	Melting Point (°C) Exp	Lit
1			92	125–126	125–127 [46]
2			88	82–83	–
3			91	76–78	78–81 [46]
4			85	Oil	–

Table 1 (continued)

Entry	Epoxide	Product	Yield ^a (%)	Melting Point (°C) Exp	Lit
5			88	168–170	168–170 [46]
6			90	106–108	110–111 [46]
7			82	126–128	127–128 [46]
8			83	Oil	–

^aIsolated yields after 6 h reaction time

^bRegio- and Stereochemistry of the reaction was verified according to [23]; the main product has been shown

Table 2 Reduction of nitrobenzene derivatives into anilines, in the presence of nanofibrous Cu (0)

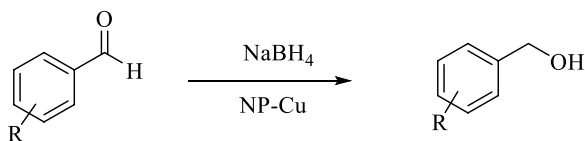
Entry	Product	Time (min)	Yield (%) ^a
1		30	98
2		35	92
3		45	93
4		45	94
5		45	90
6		90	88
7		120	84
8		40	82

^aDetermined by GC.

Experimental

General

All commercially available chemicals were purchased from Sigma-Aldrich (USA) and Merck (Germany) companies and used without further purification. Products were characterized by their physical constant and comparison with authentic samples. Reaction monitoring was accomplished by TLC on silica gel polygram SILG/

Table 3 Reduction of aromatic aldehydes into benzyl alcohols in the presence of nanofibrous Cu (0) under reflux conditions

Entry	Product	Time (min)	Yield.(%) ^a
1		30	94
2		30	92
3		30	92
4		30	96
5		30	88
6		40	84
7		30	86
8		40	91
9		60	95

^aDetermined by GC.

UV 254 plates. The IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrophotometer using KBr pellets for the samples and the catalyst in the range of 4000–400 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded in $\text{DMSO}-d_6$ on a Bruker 250 MHz spectrometer using TMS as the internal standard. Thermal stability of the supported catalyst was examined by BÄHR, SPA 503 Thermo-gravimetric Analyzer (TGA) at heating rate of 10 $^\circ\text{C min}^{-1}$ over the temperature range of 40–950 $^\circ\text{C}$. TEM images were recorded by Zeiss-EM10C-100 kV. SEM images were recorded

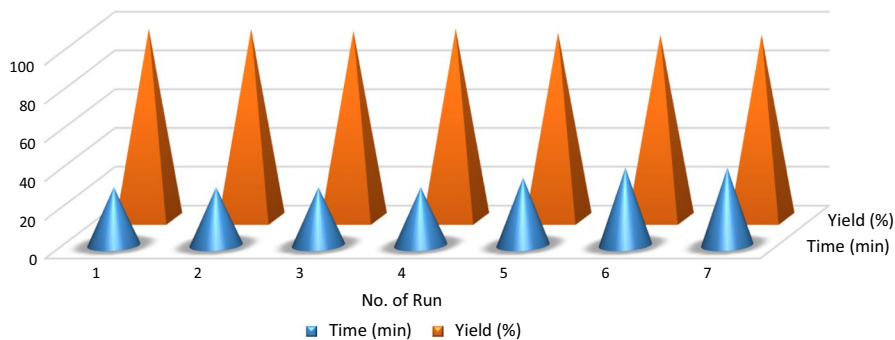


Fig. 6 The reusability of catalyst in nitrobenzene reduction, Conditions: 80 °C, 30 min

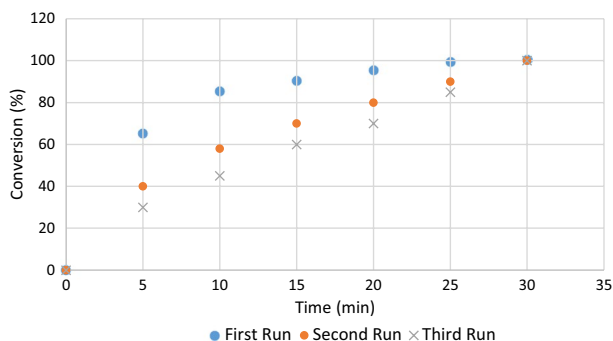


Fig. 7 Assessment of the stability of the catalyst as an indication of the progress of deactivation (e.g. the graph was drawn by the comparison of UV–visible absorption spectra for the reduction of 4-nitrophenol to 4-aminophenol. the disappearance of the absorbance of the reactant at $\lambda_{\text{max}} = 400$ nm was used as the benchmark)

Table 4 Comparison of nanofibrous copper (0) with reported catalysts in the reduction of nitrobenzene to aniline

Entry	Catalyst/Condition	Catalyst loading (g)	Time (h)	Yield (%)	Ref
1	Polymer supported Pd/NaBH ₄ , H ₂ O, RT	0.04	6	96	[48]
2	Silver @ rice husk/ NaBH ₄ , H ₂ O, reflux	0.5	0.8	95	[49]
3	Silica gel supported PEG and zinc powder/ Water, reflux	0.1	1	86	[50]
4	Fe ₃ O ₄ @nSiO ₂ @mSiO ₂ /Pr-Imi-NH ₂ -Ag/ NaBH ₄ , H ₂ O, reflux	0.02	0.75	98	[32]
5	Nanofibrous copper	0.01	0.5	98	This work

by ZEISS-FESEM-Sigma VP. XRD analysis was recorded by Panalytical X' Pert Pro. BET analysis was performed by Quantachrome.

General procedure for the preparation of nanofibrous Copper

In a 250 mL round-bottom flask, 0.5 g of Cu–Zn alloy was mixed with 0.5 g NaOH and 100 mL of distilled water at room temperature for 24 h. Afterwards, the mixture was filtered and washed with distilled water for several times. The nanofibrous copper precipitate was dried at 60 °C for 24 h.

Typical procedure for the preparation of 1,2,3-triazole derivatives

A mixture of phenyl acetylene (1 mmol), sodium azide (1 mmol), epoxide/alkyl chloride (1 mmol), nano-porous copper (0.05 g, 80 mol%) and distilled water (5 mL) was heated at reflux conditions. Completion of the reaction was indicated by TLC [acetone/n-hexane (3:10)], following which the catalyst was filtered, and the product was extracted using ethyl acetate. The organic layer was concentrated, and the product was obtained by evaporating the solvent in a rotary evaporator. Further product purifications can be done via recrystallization in an ethanol–water mixture or in the case of oily substances via column chromatography.

Typical procedure for the reduction of nitrobenzenes to anilines

A mixture of nitrobenzene derivative (1 mmol), sodium borohydride (2 mmol), nano-porous copper (0.01 g, 15 mol%) and ethanol (5 mL) was heated at reflux conditions. After completion of the reaction, as indicated by TLC [EtOAc/n-hexane (1:4)] or GC, the catalyst was filtered and the product was obtained after evaporation of ethanol. Further product purifications can be done via recrystallization in an ethanol–water mixture or in the case of oily substances via column chromatography.

Typical procedure for the reduction of aromatic aldehydes into benzyl alcohols

A mixture of aromatic aldehyde (1 mmol), sodium borohydride (2 mmol), nano-porous copper (0.01 g, 15 mol%) and ethanol (5 mL) was heated at reflux conditions. Completion of the reaction was monitored by TLC [ethyl acetate/n-hexane (1:4)] or GC, following which the catalyst was filtered, and the product was obtained after evaporation of ethanol. Further product purifications can be done via recrystallization in an ethanol–water mixture or in the case of oily substances via column chromatography.

2-Phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol (Table 1, Entry 1): Pale yellow solid; ¹HNMR(400 MHz, CDCl₃) δ 8.22 (s, 1H; NCH=C), 7.31–7.78 (m, 10 H; ArH), 4.71–4.84, 4.21–4.34 (2 m, 2H; CH₂), 3.72 (dd, ³J_{H,H}=8.7 Hz, ³J=4.7 Hz, 1H; CHCH₂), 3.36 (wide peak 1H, OH); ¹³C NMR (100 MHz, CDCl₃) δ 147.8 (NCCH), 138.1, 131.9, 129.9, 129.8, 129.5, 128.9, 128.2, 126.4, 121.6 (NCCH), 67.6 (CHCH₂), 64.7 (CH₂); IR (neat, cm⁻¹) ν 699, 765, 1050, 1073, 1124, 1275, 1379, 1456, 1497, 2939, 3032, 3087, 3123, 3478.

Conclusion

Nanofibrous copper was prepared using a simple and straightforward method that involved the dealloying of Cu–Zn alloy in an alkaline solution. This nanoporous catalyst proved useful in azide-alkyne cycloaddition reactions, reduction of nitrobenzenes to anilines, and reduction of aromatic aldehydes to benzyl alcohols. Given the satisfactory results obtained from these reactions, it can serve as an alternative nanostructured catalyst for similar organic reactions as well as functional group transformations. This catalyst showed very good results including high product yield, short reaction time and recyclability.

Acknowledgements The authors gratefully acknowledge the financial support from the Mahshahr Branch, Islamic Azad University, Iran.

References

1. Slater AG, Cooper AI (2015) Porous materials Function-led design of new porous materials. *Science* 348:e8075
2. Gottardi G, Galli E (2012) Natural zeolites (Vol. 18). Springer Science, Business Media.
3. Liu Y, O’Keeffe M, Treacy MM, Yaghi OM (2018) The geometry of periodic knots, polycatenanes and weaving from a chemical perspective: a library for reticular chemistry. *Chem Soc Rev* 47:4642
4. Zhao D, Feng J, Huo Q, Melosh N, Fredrickson GH, Chmelka BF, Stucky GD (1998) Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* 279:548
5. Zhao XS, Lu GQ, Millar GJ (1996) Advances in mesoporous molecular sieve MCM-41. *Ind Eng Chem Res* 35:2075
6. Cote AP, Benin AI, Ockwig NW, O’Keeffe M, Matzger AJ, Yaghi OM (2005) Porous, crystalline, covalent organic frameworks. *Science* 310:1166
7. Abbas A, Abbas S, Wang X (2016) Nanoporous copper: fabrication techniques and advanced electrochemical applications. *Corros Rev* 34:249
8. Zhang J, Li CM (2012) Nanoporous metals: fabrication strategies and advanced electrochemical applications in catalysis, sensing and energy systems. *Chem Soc Rev* 41:7016
9. Chen LY, Yu JS, Fujita T, Chen MW (2009) Nanoporous copper with tunable nanoporosity for SERS applications. *Adv Func Mater* 19:1221
10. Erlebacher J, Aziz MJ, Karma A, Dimitrov N, Sieradzki K (2001) Evolution of nanoporosity in dealloying. *Nature* 410:450
11. Solanki V, Krupanidhi SB, Nanda KK (2017) Sequential elemental dealloying approach for the fabrication of porous metal oxides and chemiresistive sensors thereof for electronic listening. *ACS Appl Mater Interfaces* 9:41428
12. Hayes JR, Hodge AM, Biener J, Hamza AV, Sieradzki K (2006) Monolithic nanoporous copper by dealloying Mn–Cu. *J Mater Res* 21:2611
13. Lu HB, Li Y, Wang FH (2007) Synthesis of porous copper from nanocrystalline two-phase Cu–Zr film by dealloying. *Scripta Mater* 56:165
14. Zhao C, Qi Z, Wang X, Zhang Z (2009) Fabrication and characterization of monolithic nanoporous copper through chemical dealloying of Mg–Cu alloys. *Corros Sci* 51:2120
15. Liu WB, Zhang SC, Li N, Zheng JW, Xing YL (2011) A facile one-pot route to fabricate nanoporous copper with controlled hierarchical pore size distributions through chemical dealloying of Al–Cu alloy in an alkaline solution. *Microporous Mesoporous Mater* 138:1
16. Dan Z, Qin F, Sugawara Y, Muto I, Hara N (2012) Fabrication of nanoporous copper by dealloying amorphous binary Ti–Cu alloys in hydrofluoric acid solutions. *Intermetallics* 29:14
17. Aburada T, Fitz-Gerald JM, Scully JR (2011) Synthesis of nanoporous copper by dealloying of Al–Cu–Mg amorphous alloys in acidic solution: The effect of nickel. *Corros Sci* 53:1627
18. Dan Z, Qin F, Makino A, Sugawara Y, Muto I, Hara N (2014) Fabrication of nanoporous copper by dealloying of amorphous Ti–Cu–Ag alloys. *J Alloy Compd* 586:S134

19. Tornøe CW, Christensen C, Meldal M (2002) Peptidotriazoles on solid phase:[1,2,3]-triazoles by regioselective copper (I)-catalyzed 1, 3-dipolar cycloadditions of terminal alkynes to azides. *J Org Chem* 67:3057
20. Appukkuttan P, Dehaen W, Fokin VV, Van der Eycken E (2004) A microwave-assisted click chemistry synthesis of 1, 4-disubstituted 1, 2, 3-triazoles via a copper (I)-catalyzed three-component reaction. *Org Lett* 6:4223
21. Feldman AK, Colasson B, Fokin VV (2004) One-pot synthesis of 1, 4-disubstituted 1, 2, 3-triazoles from in situ generated azides. *Org Lett* 6:3897
22. Spiteri C, Moses JE (2010) Copper-catalyzed azide–alkyne cycloaddition: regioselective synthesis of 1, 4, 5-trisubstituted 1, 2, 3-triazoles. *Angew Chem Int Ed* 49:31
23. Alonso F, Moglie Y, Radivoy G, Yus M (2011) Multicomponent click synthesis of 1, 2, 3-triazoles from epoxides in water catalyzed by copper nanoparticles on activated carbon. *J Org Chem* 76:8394
24. Tafesh AM, Weiguny J (1996) A review of the selective catalytic reduction of aromatic nitro compounds into aromatic amines, isocyanates, carbamates, and ureas using CO. *Chem Rev* 96:2035
25. Herves P, Pérez-Lorenzo M, Liz-Marzán LM, Dzubiella J, Lu Y, Ballauff M (2012) Catalysis by metallic nanoparticles in aqueous solution: model reactions. *Chem Soc Rev* 41:5577
26. Burge HD, Collins DJ, Davis BH (1980) Intermediates in the Raney nickel catalyzed hydrogenation of nitrobenzene to aniline. *Ind Eng Chem Prod Res Dev* 19:389
27. Spencer J, Anjum N, Patel H, Rathnam RP, Verma J (2007) Molybdenum hexacarbonyl and DBU reduction of nitro compounds under microwave irradiation. *Synlett* 2007:2557
28. Skupiń J, Zukowska A, Chajewski A (2001) Reduction of nitrobenzene to aniline with carbon monoxide and water in the presence of the PdCl₂/Fe/I₂ system. *React Kinet Catal Lett* 72:21
29. Makarova OV, Rajh T, Thurnauer MC, Martin A, Kemme PA, Cropek D (2000) Surface modification of TiO₂ nanoparticles for photochemical reduction of nitrobenzene. *Environ Sci Technol* 34:4797
30. Subramanian T, Pitchumani K (2012) Selective reduction of nitroarenes by using zeolite-supported copper nanoparticles with 2-propanol as a sustainable reducing agent. *ChemCatChem* 4:1917
31. Roy P, Periasamy AP, Liang CT, Chang HT (2013) Synthesis of graphene-ZnO-Au nanocomposites for efficient photocatalytic reduction of nitrobenzene. *Environ Sci Technol* 47:6688
32. Nasab MJ, Kiasat AR (2016) Multifunctional Fe₃O₄@nSiO₂/mSiO₂/Pr-Imi-NH₂: Ag core-shell microspheres as highly efficient catalysts in the aqueous reduction of nitroarenes: improved catalytic activity and facile catalyst recovery. *RSC Adv* 6:41871
33. Gholinejad M, Zareh F, Nájera C (2018) Nitro group reduction and Suzuki reaction catalysed by palladium supported on magnetic nanoparticles modified with carbon quantum dots generated from glycerol and urea. *Appl Organomet Chem* 32:e3984
34. Mullangi D, Chakraborty D, Pradeep A, Koshti V, Vinod CP, Panja S, Vaidhyanathan R (2018) Heterogenous Catalysts: highly stable cof-supported Co/Co(OH)₂ nanoparticles heterogeneous catalyst for reduction of nitrile/nitro compounds under mild conditions. *Small* 14:1870169
35. Cantillo D, Moghaddam MM, Kappe CO (2013) Hydrazine-mediated reduction of nitro and azide functionalities catalyzed by highly active and reusable magnetic iron oxide nanocrystals. *J Org Chem* 78:4530
36. Ghonchepour E, Islami MR, Bananezhad B, Mostafavi H, Tikdari AM (2019) Synthesis of recoverable palladium composite as an efficient catalyst for the reduction of nitroarene compounds and Suzuki cross-coupling reactions using sepiolite clay and magnetic nanoparticles (Fe₃O₄@sepiolite-Pd²⁺). *C R Chim* 22:84
37. Zhu H, Ke X, Yang X, Sarina S, Liu H (2010) Reduction of nitroaromatic compounds on supported gold nanoparticles by visible and ultraviolet light. *Angew Chem Int Ed* 49:9657
38. Chakraborty S, Bhattacharya P, Dai H, Guan H (2015) Nickel and iron pincer complexes as catalysts for the reduction of carbonyl compounds. *Acc Chem Res* 48:1995
39. Kidwai M, Bansal V, Saxena A, Shankar R, Mozumdar S (2006) Ni-nanoparticles: an efficient green catalyst for chemoselective reduction of aldehydes. *Tetrahedron Lett* 47:4161
40. Subramanian T, Pitchumani K (2012) Transfer hydrogenation of carbonyl compounds and carbon-carbon multiple bonds by zeolite supported Cu nanoparticles. *Catal Sci Technol* 2:296
41. Rayhan U, Do JH, Arimura T, Yamato T (2015) Reduction of carbonyl compounds by Raney Ni–Al alloy and Al powder in the presence of noble metal catalysts in water. *C R Chim* 18:685
42. Naimi-Jamal MR, Mokhtari J, Dekamin MG, Kaupp G (2009) Sodium tetraalkoxyborates: intermediates for the quantitative reduction of aldehydes and ketones to alcohols through ball milling with NaBH₄. *Eur J Org Chem* 2009:3567

43. Sayyahi S, Saghanezhad SJ (2019) Copper-Based Bulk and Nano-Catalysts for the One-Pot Propargylamine Synthesis. *Mini-Rev Org Chem* 16:361
44. Tappan BC, Steiner SA III, Luther EP (2010) Nanoporous metal foams. *Angew Chem Int Ed* 49:4544
45. Gao W, Hood ZD, Chi M (2017) Interfaces in heterogeneous catalysts: advancing mechanistic understanding through atomic-scale measurements. *Acc Chem Res* 50:787
46. Salamatmanesh A, Miraki MK, Yazdani E, Heydari A (2018) Copper (I)–caffeine complex immobilized on silica-coated magnetite nanoparticles: a recyclable and eco-friendly catalyst for click chemistry from organic halides and epoxides. *Catal Lett* 148:3257
47. Scott SL (2018) A Matter of life (time) and death. *ACS Catal* 8:e8597
48. Dell'Anna MM, Intini S, Romanazzi G, Rizzuti A, Leonelli C, Piccinni F, Mastroianni P (2014) Polymer supported palladium nanocrystals as efficient and recyclable catalyst for the reduction of nitroarenes to anilines under mild conditions in water. *J Mol Catal A: Chem* 395:307
49. Davarpanah J, Kiasat AR (2013) Catalytic application of silver nanoparticles immobilized to rice husk-SiO₂-aminopropylsilane composite as recyclable catalyst in the aqueous reduction of nitroarenes. *Catal Commun* 41:6
50. Keshipour S, Adak K (2018) Reduction of Nitroaromatics to Amines with Cellulose Supported Bimetallic Pd/Co Nanoparticles. *Iran J Chem Chem Eng* 37:23

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.