FULL PAPER



Cu nanoparticles immobilized on modified magnetic zeolite for the synthesis of 1,2,3-triazoles under ultrasonic conditions

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Mehdi Bakavoli, Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, 91775 -1436, Iran. Email: mbakavoli@um.ac.ir Magnetically recoverable copper nanoparticle-loaded natural zeolite (CuNPs/ MZN) as an efficient catalyst was synthesized. The Fe_3O_4 magnetic nanoparticles were immobilized into the pores of natural clinoptilolite zeolite, which were modified with epichlorohydrine and ethylenediamine species and then CuNPs were decorated on the surface of functionalized zeolite (CuNPs/ catalysts were successfully characterized MZN). The by Fourier transform-infrared, CHN, thermogravimetric analysis, inductively coupled plasma, X-ray diffraction, scanning electron microscopy and transmission electron microscopy techniques. The 1,2,3-triazoles were readily synthesized through using the catalyst in high yields and short reaction times under ultrasonic conditions via CuAAC reactions of aryl azides and terminal alkynes. The CuNPs/MZN was easily separated from the reaction mixture by an external magnet and reused several times successfully. The catalyst could be used for the synthesis of various organic compounds.

KEYWORDS

1,2,3-triazoles, clinoptilolite, Cu nanoparticles, magnetic zeolite, nanocomposite

1 | INTRODUCTION

1,2,3-Triazoles have been widely used in many aspects of human activities, such as industry, pharmacy, medical, biology, agriculture, etc. Their applications in industry are in the synthesis of dyes, photographic materials and corrosion inhibition. These compounds are present in some agrochemicals, and also have many applications in the synthesis of pharmaceutical compounds such as anti-cancer, anti-bacterial and anti-HIV drugs.^[1-4]

One of the most efficient and widely used methodologies for selective C–N bond-forming reactions is click chemistry, coined by Sharpless and Fokin, 'click chemistry' offers extremely regioselective synthesis of 1,4-disubstituted-1,2,3-triazoles with high yields.^[5] These useful materials have been prepared using two methods, thermal 1,3-dipolar Huisgen cycloaddition^[6] and CuAAC reaction.^[7]

There are many disadvantages in thermal 1,3-dipolar Huisgen cycloaddition, one of them is making two isomers.^[8] That is why this reaction is not common in chemical synthesis. It might be desirable to develop a new regioselective synthesis, using Cu (0) catalyst. The CuAAC reaction was developed as a modification for Huisgen reaction defects.^[9] As was observed by Meldal and co-workers, this chemical ligation of azides and terminal alkynes delivered exclusively the 1,4-disubstituted 1,2,3-triazoles.^[10]

The required copper (0,I) catalysts are usually prepared by *in situ* reduction of copper (II) salts with sodium ascorbate^[11] or NaBH₄.^[12] In recent studies, the CuAAC has been proven to be accelerated by immobilizing copper species on a large variety of solid 2 of 9 WILEY Organometallic Chemistry

supports,^[13] such as charcoal,^[14] silica,^[15] zeolite^[16] and polymers.^[17,18] However, the immobilized catalysts are difficult to separate from the solution, only through the use of filter, high-speed centrifugation or precipitation. An ideal solution to this problem is using the magnetic property.^[19]

Metal nanoparticles are very attractive catalysts compared with bulk catalysts as they have a high surface to volume ratio and their surface atoms are very active.^[20] Numerous review articles highlight the use of many different types of organic and inorganic reactions of noble metal nanoparticles suspended in colloidal solutions as well as those adsorbed onto different supports as catalysts.^[21] Copper and copper oxide nanoparticles are of significant technological interest.^[22] Copper, in the nanoform, has been known for the past decade to show fascinating catalytic activity for the various organic reactions.^[23] Cu nanoparticles are of great interest in a broad technological arena including catalysis and energy conversion.^[24]

Ultrasound-assisted organic synthesis, as a synthetic approach, is a powerful technique that is used to accelerate organic reactions. The notable features of the ultrasound approach are enhanced reaction rates, formation of pure products in high yields, and easier manipulation.^[25,26] Ultrasound has been recognized as an important technique for green and sustainable synthetic processes.^[27]

Natural or synthetic zeolites^[28] are microporous aluminosilicate mineral compounds that are widely used as waste water and gas treatment, catalysts, molecular sieve, and also in nuclear processing, agriculture, advanced materials, and recently as nanocomposites in organic synthesis.^[29,30] Magnetic zeolites have been produced by modifying their surface and inner pores with a magnetic component.^[31] Use of magnetic adsorbents provides easier separation and avoids tedious and time consuming work-ups.^[32] Recently, green zeolite/Fe₃O₄ nanocomposites have been synthesized, characterized^[33] and used in organic transformations.

In continuation of our success in the synthesis of organic compounds via multi-component reactions,^[34–36] in this report we present the results of an extended investigation on the activity of the clinoptilolite/Fe₃O₄ nanocomposite containing immobilized Cu (0) nanoparticles (CuNPs/MZN) in the synthesis of propargylamines,^[36] as an efficient and powerful catalyst for the synthesis of 1,2,3-triazoles derivatives that facile separation of the catalyst using an external magnet, and the recyclability of the catalyst (up to five times) is one of the other important benefits of this system. To the best of our knowledge, there are no examples of the use of zeolite nanomagnetic catalysts, especially Cu decorated on functionalized magnetic



1a: R= Ph, **1b:** R= 4-NO₂Ph, **1c:** R= 4-BrPh, **1d:** R= 4-CH₃Ph, **1e:** R= 4-ClPh, **1f:** R= PhCH₂ **2a:** R_1 = Ph, **2b:** R_1 = CH₂OH, **2c:** CH₂Br

SCHEME 1 Synthesis of 1,2,3-triazoles in the presence of nanomagnetic catalyst (CuNPs/MZN)

zeolite as a catalyst for the synthesis of 1,2,3-triazoles derivatives (Scheme 1).

2 | EXPERIMENTAL

2.1 | Chemicals

All solvents were purchased from Merck. Natural clinoptilolite zeolite was purchased from Afrazand, Semnan, Iran. Iron (III) chloride hexahydrate, iron (II) chloride tetrahydrate, sodium hydroxide, copper (II) acetate, sodium borohydride, ethylene glycol, ethanol, hydrochloric acid and other compounds were obtained from Sigma-Aldrich in analytical grade and used without further purification.

2.2 | Apparatus

The melting point of the products was determined with an Electrothermal Type 9100 melting point apparatus. The Fourier transform-infrared (FT-IR) spectra were recorded on an Avatar 370 FT-IR Thermal Nicolet spectrometer. Mass spectra were recorded on a 5973 Network Mass Selective Detector. ¹H-NMR and ¹³C-NMR spectra were measured (CDCl₃) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively. Thermogravimetric analysis (TGA) was performed on a Shimadzu Thermogravimetric Analyzer (TG-50). Transmission electron microscope (TEM) images were acquired on a TEM microscope Leo 912 AB120 KV Zeiss, Germany. Inductively coupled plasma was obtained using a Varian, VISTA-PRO, CCD, Australia. X-ray diffraction (XRD) patterns were collected using a Braker D4 X-ray diffractometer with Ni-filtered Cu KR radiation (40 kV, 30 MA). Elemental analysis was carried out using CHNS (O) Analyzer Model FLASH EA 1112 series made by Thermo Finnigan.

2.3 | Catalyst preparation

Based on our previous report,^[36] the magnetic zeolite nanocomposite (Zeolite/Fe₃O₄) was synthesized by a chemical co-precipitation technique using ferric and

ferrous ions, and followed by preparation of functionalized magnetic nanocomposite of clinoptilolite zeolite with epichlorohydrine and ethylenediamine linker, and then *in situ* generation of CuNPs on the surface of composite (Scheme 2).

2.4 | Synthesis of 1,2,3-triazoles via the reaction of aryl azide and terminal alkyne

To a solution of aryl azide (1.1 mmole), terminal alkyne (1.0 mmole) in a mixture of H₂O/EtOH (1:1; 2 mL), CuNPs/MZN catalyst (10.0 mg) was added and the mixture was stirred at 50°C for 0.5-3 hr. The progress of the reaction was monitored by thin-layer chromatography and, upon completion of the reaction, the reaction mixture was diluted with EtOAc and the catalyst was removed by an external magnet, washed with acetone and dried overnight to be ready for the next run. The organic layer was dried over anhydrous Na₂SO₄, followed by evaporation under reduced pressure to remove the solvent. The residue was purified by recrystallization from ethanol to afford corresponding 1,2,3-triazole. The product was identified by melting point, CHN, mass spectrometrv. ¹H-NMR and ¹³C-NMR spectroscopy (See Supporting Information).

2.4.1 | 1-(4-diphenyl)-1H-1,2,3-Triazole (Table 2, entry 1)

Pale yellow solid, m.p.: 183–184°C. ¹H-NMR (300 MHz, CDCl₃): δ = 7.28–7.81 (m, 6H), 7.93 (d, 2H), 8.22 (d, 2H), 8.52 (s, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 148.3, 136.9, 130.1,129.6, 128.8, 128.6, 128.3, 125.7, 120.4, 117.5.

2.4.2 | 1-(4-nitrophenyl)-4-Phenyl-1,2,3-triazole (Table 2, entry 2)

Orange solid, m.p.: 254–255°C. ¹H-NMR (300 MHz, DMSO-d₆), $\delta = 7.34$ (t, 1H), 7.51 (t, 2H), 7.99 (m, 2H), 8.30 (m, 2H), 8.53 (m, 2H), 9.57 (s, 1H). ¹³C-NMR (75 MHz, DMSO-d₆), $\delta = 120.4$, 120.9, 125.9, 126.1, 128.4,

129.0, 129.5, 130.2, 141.3, 147.1, 148.3. MS: m/z (%) = 266 (M+).

2.4.3

1-(4-bromophenyl)-4-Phenyl-1H-1,2,3-triazole (Table 2, entry 3)

White solid, m.p.: 232–234°C. ¹H-NMR (CDCl₃, 300 MHz), $\delta = 7.35-7.91$ (m, 9H), 8.17 (s, 1H); ¹³C-NMR (75 MHz, CDCl₃), $\delta = 117.2$, 121.7, 122.3, 125.7, 128.5, 128.7, 128.8, 129.8, 130.8, 132.8, 135.9.

2.4.4 | 4-Phenyl-1-p-tolyl-1,2,3-triazole (Table 2, entry 4)

White solid, m.p.: 174–175°C. ¹H-NMR (CDCl₃, 300 MHz), $\delta = 2.42$ (s, 3H), 7.32 (m, 3H), 7.44 (t, 2H), 7.65 (d, 2H), 7.90 (m, 2H), 8.14 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃), $\delta = 21.0$, 117.6, 120.4, 125.8, 128.3, 128.8, 130.2, 130.3, 134.7, 138.8, 148.2. MS: m/z (%) = 235 (M+).

2.4.5

1-(4-chlorophenyl)-4-Phenyl-1H-1,2,3-triazole (Table 2, entry 5)

Yellow solid, m.p.: 227–229°C. ¹H-NMR (300 MHz, CDCl₃), $\delta = 7.40-7.74$ (m, 5H), 7.95–8.03 (M, 4H), 9.34 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃), $\delta = 120.17$, 122.14, 125.84, 128.83, 129.51, 130.40, 130.54, 133.46, 135.89, 147.95.

2.4.6 | 1-(phenyl)-1H-1,2,3-Triazole-4-yl-methanol (Table 2, entry 6)

White solid, m.p.: 115–118°C. ¹H-NMR (DMSO-d₆, 300 MHz), $\delta = 4.73$ (1H, d), 5.46 (td, 2H), 7.56–7.62 (m, 1H), 7.68–7.73 (m, 2H), 8.00–8.03 (m, 2H), 8.77 (s, 1H). ¹³C-NMR (DMSO-d₆, 75 MHz), $\delta = 55.7$, 120.6, 121.6, 129.1, 130.5, 137.4, 149.8.



SCHEME 2 Preparation of nanomagnetic catalyst (CuNPs/MZN)

MZN

CuNPs/MZN

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2.4.7 | 1-(4-nitrophenyl)-1H-1,2,3-Triazole-4-yl-methanol (Table 2, entry 7)

White solid, m.p.: 201–202°C. ¹H-NMR (DMSO-d₆, 300 MHz), $\delta = 4.63$ (s, 2H), 5.52 (s, 1H), 8.05–8.08 (d, 2H), 8.24–8.27 (d, 2H), 8.72 (s, 1H). ¹³C-NMR (DMSO-d₆, 75 MHz), $\delta = 55.31$, 120.42, 121.49, 125.67, 141.17, 146.65, 150.13.

2.4.8 | [1-(4-bromo-phenyl)-1H-[1,2,3] triazol-4-yl]-Methanol (Table 2, entry 8)

Yellowish solid, m.p.: 134–135°C. ¹H-NMR (300 MHz, CDCl₃), δ = 4.67 (s, 2H), 5.56 (s, 2H), 7.63–7.81 (m, 4H), 8.61 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃), δ = 55.42, 121.30, 121.56, 122.08, 133.09, 136.21, 149.65.

2.4.9

1-(4-methylphenyl)-1H-1,2,3-triazole-4-yl-Methanol (Table 2, entry 9)

White solid, m.p.: 125–127°C. ¹H-NMR (DMSO-d₆, 300 MHz), $\delta = 2.28$ (s, 3H), 4.66 (d, 2H), 5.48 (s, 1H), 7.65 (d, 2H), 7.99 (d, 2H), 8.89 (s, 1H). ¹³C-NMR (DMSO-d₆, 75 MHz), $\delta = 21.1$, 59.0, 120.0, 121.6, 130.9, 132.7, 135.3, 150.4.

2.4.10 | 1-(4-chlorophenyl)-1H-1,2,3-triazole-4-yl-Methanol (Table 2, entry 10)

White solid, m.p.:144–146°C. ¹H-NMR (DMSO-d₆, 300 MHz), $\delta = 4.67$ (d, 2H), 5.54 (t, 1H), 7.53–7.56 (d, 2H), 7.86–7.89 (d, 2H), 8.62 (s, 1H). ¹³C-NMR (DMSO-d₆, 75 MHz), $\delta = 54.38$, 121.38, 121.87, 130.12, 133.24, 135.84, 149.67.

2.4.11 | 1-Benzyl-4-phenyl-1H-1,2,3-triazole (Table 2, entry 12)

¹H-NMR (CDCl₃, 300 MHz), $\delta = 5.63$ (s, 2H), 7.30–7.37 (m, 3H), 7.42–7.45 (m, 5H), 7.70 (s, 1H), 7.83–7.85 (m, 2H). ¹³C-NMR (CDCl₃, 75 MHz), $\delta = 54.27$, 119.47, 125.72, 128.09, 128.19, 128.7, 128.82, 129.19, 130.56, 134.71, 148.28. MS: m/z (%) = 235 (M+). Anal. calcd for C₁₅H₁₃N₃ (235.284): C, 76.57; H, 5.57; found: C, 76.40; H, 5.69.

2.4.12 | 1-Benzyl-1H-1,2,3-triazol-4-yl-methanol (Table 2, entry 13)

White solid, m.p. 75–78°C. ¹H-NMR (300 MHz, DMSO-d₆), δ = 4.58 (s, 2H), 5.56 (s, 2H), 7.20–7.30 (m, 5H), 8.15 (s, 1H). ¹³C-NMR (75 MHz, DMSO-d₆), δ = 53.40, 55.22, 123.66, 128.46, 128.66, 129.18, 136.14, 148.26.

3 | RESULTS AND DISCUSSION

As shown in Scheme 2, CuNPs/MZN catalyst was prepared in three steps. First, the MZN was synthesized by green quick precipitation method and epichlorohydrine– ethylenediamine covalently bonded to negative oxygen related to aluminosilicate groups on the surface of zeolite or hydroxyl groups of Fe₃O₄ NPs.^[36] Later, the ligands were activated with NaOH solution in EtOH and treated with copper (II) acetate, which was complexed to N, N and O available on linker and zeolite. Finally, Cu (II) nanoparticles were reduced to Cu (0) with NaBH₄ as reductant.^[43]



FIGURE 1 Fourier transform-infrared (FT-IR) (down to up) (a) zeolite, (b) magnetic zeolite (MZ), (c) MZE, (d) MZN, (e) CuNPs/MZN



FIGURE 2 Energy-dispersive X-ray (EDS) analysis of final catalyst (CuNPs/MZN)

The prepared catalyst, CuNPs/MZN, was characterized by FT-IR, TGA, scanning electron microscopy (SEM), TEM, energy-dispersive X-ray (EDX), XRD, and vibrating-sample magnetometer (VSM).

FT-IR spectroscopy was used for characterization of the catalyst structure (Figure 1). The FT-IR spectrum of clinoptilolite is dominated by some of the major zeolite



FIGURE 3 (a) The scanning electron microscopy (SEM) image of CuNPs/MZN. (b) The transmission electron microscopy (TEM) image of CuNPs/MZN



FIGURE 4 Thermogravimetric analysis (TGA) analysis of MZN

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framework bands in the range of 720–790 cm⁻¹ υ_s (Si-O), 1020 cm⁻¹ (Si-OH), 1130 cm⁻¹ υ_{as} (Si-O and Al-O) and 3550 cm⁻¹ for isolated silanol (Si-OH) (Figure 1a).^[44]

The strong adsorption bands at 573 cm^{-1} can be attributed to the stretching vibration of the Fe-O band, which confirms the presence of Fe₃O₄ nanoparticles (Figure 1b–d).^[45] The broad absorption band at 3444 cm ⁻¹ is related to the stretching vibration of OH, demonstrating the presence of hydroxyl groups on the surface



FIGURE 5 Magnetization curve of CuNPs/MZN

TABLE 1 Optimization of solvent, temperature and amount ofcatalyst

Entry	Solvent	Catalyst (mg)	Temp. (°C)	Time (hr)	Yield (%) ^a
1	H ₂ O	_	rt	24	Trace
2	МеОН	-	rt	24	Trace
3	EtOH	-	rt	24	Trace
4	n-hexane	-	rt	24	Trace
5	H ₂ O/EtOH (1:1, 2 mL)	_	rt	24	Trace
6	H ₂ O	5	rt	10	12
7	МеОН	5	rt	10	15
8	EtOH	5	rt	10	18
9	n-hexane	5	rt	10	Trace
10	H ₂ O/MeOH (1:1, 2 mL)	5	rt	10	30
11	H ₂ O/EtOH (1:1, 2 mL)	10	30	10	45
12	H ₂ O/EtOH (1:1, 2 mL)	10	40	10	60
13	H ₂ O/EtOH (1:1, 2 mL)	10	50	5	85
14	H ₂ O/EtOH (1:1, 2 mL)	10	50	2.5	93
15	H ₂ O/EtOH (1:1, 2 mL)	10	80	2.5	93
16	H ₂ O/EtOH (1:1, 2 mL)	10	50	2	98 ^b

^aBased on isolated yield.

^bUnder ultrasonic conditions.

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TABLE 2 Synthesis of 1,2,3-triazoles 3a-n using CuNPs/MZN as catalyst^a

Entry	R	R ₁	Product ^b	Time (hr)	Yield (%) ^c	Melting point (°C)	
						Found	Reported
1	1a	Ph		2	91	183–184	181–183 ^[37]
2	1b	Ph		2	98	254–255	254 ^[37]
3	1c	Ph	N=N N	2	95	232–234	232 ^[37]
4	1d	Ph	H ₃ C	2.5	90	174–175	174 ^[37]
5	1e	Ph		3	96	227-229	228 ^[37]
6	1a	CH ₂ OH	N OH	2	95	115–118	116-118 ^[38]
7	1b	CH ₂ OH	N O ₂ N O ₂ N O _H	3	90	201–202	201-202 ^[38]
8	1c	CH ₂ OH	N=N OH	2.5	90	134–135	135–137 ^[39]
9	1d	CH ₂ OH	N=N OH	3	91	125–127	124–125 ^[40]
10	1e	CH ₂ OH		2.5	90	144–146	144–145 ^[41]
11	1b	CH ₂ Br	N Br	3	91	151–153	152–154 ^[42]
12	1f	Ph		0.5	96	128-130	129–131 ^[40]
13	1f	CH ₂ OH	N=N OH	0.75	95	75–78	75–77 ^[41]
14	1f	CH ₂ Br	N=N N-Br	1	95	123-125	124-126 ^[42]

^aReaction conditions: azides (**2a–f**; 1.1 mmol), terminal alkynes (**2a–c**; 1 mmol), CuNPs/MZN MNPs (3 mol %), 50°C in EtOH:H₂O (1:1). ^bThe known products were identified by comparing their melting points and ¹H-NMR and ¹³C-NMR. ^cIsolated yields.

of materials (Figure 1a–e). The epoxy rings that are anchored on the surface of zeolite and Fe_3O_4 composite, (MZE), are characterized by the methylene C-H

stretching at 2950 cm⁻¹ and C-O-C vibration stretching at 1240–1260 cm⁻¹. The bonds at 3436 and 3700 cm⁻¹ are due to stretching of the NH₂, and N-H bonds or

overtone peaks of C-O stretching bonds at 1233 cm^{-1} at MZN (Figure 1d). In all cases, vibration frequency was covered by the broad band of stretching vibration O-H and asymmetric vibration of the Si–O–Si and Al-O-Al bonds, respectively. The decreased intensity of the vibration band at 3400–3700 cm⁻¹ of CuNPs/ MZN can be attributed to the coordination of Cu nanoparticles to N, N and O species, which are available on the surface of the composite.^[45] The elemental analysis obtained from the EDS analysis confirms the existence of all elements (Fe, Si, Al, O, Na, K, Cu, Ca) in structures of catalyst (Figure 2).

The morphological features were studied using the SEM technique. The SEM image of CuNPs/MZN (Figure 3a) demonstrates that these modified copper-loaded MZ NPs are almost spherical, in aggregated form due to the magnetic nature of catalyst. Also, the particle size of CuNPs/MZN was studied using the TEM technique. The TEM image of the sample (Figure 3b) shows that the average sizes of Fe_3O_4 and CuNPs are approximately between 10 and 15 nm in diameter.

The thermal stability of the MZN was characterized by TGA. The TGA curve in Figure 4 demonstrates the weight loss up to 200°C that was related to the loss of absorbed water molecules on the support or trapped water (nearly 10%) in the inner pores of zeolite. The second weight loss is related to the decomposition of organic compounds in the temperature range of 190–600°C.^[45] Therefore, the result confirms that the ligand was grafted successfully.

The magnetic behavior of CuNPs/MZN was proved by VSM. As illustrated in Figure 5, the value of the saturation magnetic moment of the catalyst is $22 \text{ em}\mu \text{ g}^{-1}$, which indicates the catalyst is super-paramagnetic.

The catalytic performance of the novel CuNPs/MZN as an efficient magnetic nanocatalyst was investigated for the synthesis of 1,2,3-triazoles compounds via click reactions. After determining the molar ratios of reactants based on mechanistic investigations and previously reported literatures, the other reaction conditions such as solvent, amount of catalyst and temperature were optimized.

In order to optimize the amount of catalyst, solvent and temperature, the reaction of 4-nitrophenyl azide and phenyl acetylene was selected as a model reaction. At first, this reaction was also carried out in the absence and presence of different amounts of catalyst (Table 1). No product was obtained in the absence of the catalyst in some polar and non-polar solvents after 24 hr (Table 1, entries 1–5). Increasing the amount of catalyst to 10 mg improved the yield of the reaction (entries 6– 14). Also, the reaction was carried out in polar solvents better than aprotic and non-polar solvents. Finally, the highest yield was obtained when the reaction was performed in a mixture of EtOH and H_2O with the ratio 1:1 in the presence of 10 mg of catalyst at 50°C (entry 14). Moreover, ultrasonic conditions have been selected for the model reaction, and the yield of the reaction was greater than under non-ultrasound conditions (entry 16).

Using these optimized reaction conditions, the scope of the reaction was extended to various azides and different terminal alkynes. According to the results shown in Table 2, all aryl azides carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in high yields within a short reaction time. Benzyl azide compared with phenyl azides required shorter reaction time (entries 12–14). Both the aromatic



FIGURE 6 Recycling experiment for catalyst



FIGURE 7 Transmission electron microscopy (TEM) photograph of CuNPs/MZN after five consecutive cycles



SCHEME 3 Proposed mechanism for the synthesis of 1,2,3-triazoles in the presence of nanomagnetic catalyst

and aliphatic terminal acetylenes gave the corresponding triazoles in excellent yields and high purity.

3.1 | Stability and reusability of catalyst

Although a small amount of catalyst (10.0 mg) was utilized, it could easily be filtered and recovered by using a magnet on the outer wall of the container (after addition of acetone) and reused. Good catalyst performance in the coupling of aryl azide and terminal alkyne was observed over five consecutive cycles (Figure 6). The TEM images of catalyst after five reuses (recovered) were studied. As shown in Figure 7, the TEM photograph of the recovered nanocatalyst shows that the structure of the catalyst remains almost the same after five reuses. In addition, the weight of the recovered catalyst is the same as the amount of fresh catalyst used the first time in the reaction.

3.2 | Suggested mechanism for preparation of 1H-1,2,3-triazoles

Under our conditions, the presence of CuNPs on the surface of magnetic natural zeolite (MZ) probably acts as the catalyst. A tentative reaction mechanism for the synthesis of 1H-1,2,3-triazoles catalyzed by CuNPs under heterogeneous conditions is proposed in Scheme 3. It is proposed that, in the first step, a terminal alkyne is coordinated to CuNPs supported on zeolite, which activates the C–H bond. As a result, the corresponding copper–alkylidine complex is formed on the surface of the nanocomposite. This is a very favorable step because Cu metal is well known to exhibit high alkynophilicity for terminal alkynes. In the second step, synthesized aryl azides attack the copper-alkylidine complex followed by intramolecular cyclization, finally leading to formation of a five-membered ring of triazole as a product.

4 | **CONCLUSIONS**

Eco-friendly CuNPs/MZN proved to be an efficient catalyst for the synthesis of 1,2,3-triazoles from aryl azide and terminal alkynes. This efficient catalyst could be easily recycled by means of an external magnet and reused without significant loss of catalytic activity for five cycles. The advantages of this catalyst compared with previously synthesized catalysts are easier work-up due to its magnetism and low reaction time. Based on preliminary mechanistic investigations, this reaction proceeds through the combination of aryl azide as an intermediate and the Cu-acetylide that is formed by zeolite assistance.

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