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Article

Harnessing the Untapped Catalytic Potential of a $CoFe_2O_4$/Mn-BDC Hybrid MOF Composite for Obtaining a Multitude of 1,4-Disubstituted 1,2,3-Triazole Scaffolds

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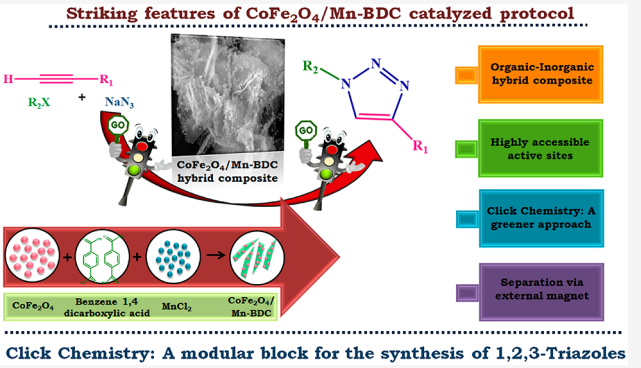
ABSTRACT: Metal−organic frameworks derived nanostructures with extraordinary variability, and many unprecedented properties have recently emerged as promising catalytic materials to address the challenges in the field of modern organic synthesis. In this contribution, the present work reports the fabrication of an intricately designed magnetic MOF composite based on Mn-BDC (manganese benzene-1,4-dicarboxylate/manganese terephthalate) microflakes via a facile and benign in situ solvothermal approach. Structural information about the as-synthesized hybrid composite has been obtained with characterization techniques such as TEM, SEM, XRD, FT-IR, AAS, EDX, ED-XRF, and VSM analysis. Upon investigation of catalytic performance, the resulting material unveils remarkable efficacy toward facile access of a diverse array of pharmaceutically active 1,2,3-triazoles from a multicomponent coupling reaction of terminal alkynes, sodium azide, and alkyl or aryl halides as coupling partners. In addition to a wide substrate scope, the catalyst with highly accessible active sites also possesses a stable catalytic metal center along with superb magnetic properties that facilitate rapid and efficient separation. The prominent feature that makes this protocol highly desirable is the ambient and greener reaction conditions in comparison to literature precedents reported to date. Further, a plausible mechanistic pathway is also proposed to rationalize the impressive potential of the developed catalytic system in the concerned reaction. We envision that findings from our study would not only provide new insights into the judicious design of advanced MOF based architectures but also pave the way toward greening of industrial manufacturing processes to tackle critical environmental and economic issues.



INTRODUCTION

The pioneering and seminal discovery of metal organic frameworks by a renowned chemist, Omar Yaghi, has sparked tremendous fascination among the scientific community worldwide. Ever since, research on the fundamental design and exploration of this intriguing class of materials continues to expand at an impressive pace.[1−7] This upsurge of interest can be predominantly attributed to the possibility of modifying the organic as well as inorganic building blocks that provide invincible strategies to produce the controlled targeted MOFs.[8−10] In addition, the phenomenal substructure of MOFs also endows them with several other marvelous attributes such as facile variability of the pore size, assorted topologies, unprecedented high surface area, and large pore volumes.[11,12] Owing to the aforementioned remarkable aspects, these unique architectures greatly revolutionized the diverse emerging disciplines of catalysis, adsorption, gas storage, sensing, and separation.[13−16] In particular, MOF based materials have marked a significant breakthrough in the arena of heterogeneous catalysis since their crystal chemistry prevents deactivation of the catalytic system as a result of the well separated arrangement of metal clusters by organic ligands that accentuate their enduring efficiency.[17−25] Indeed, integration of MOFs' functional properties with the magnetic properties of nanoparticles to obtain hybrid materials has aroused broad interest, as it not only dramatically enhances catalytic performance and durability but also facilitates expedient separation under the influence of external magnetic forces.[26−31] Driven by such innovations, tremendous endeavors are directed toward the quest of novel catalysts to improve previously unexplored organic transformations. In this context, a comprehensive literature survey reveals the scope of advancement in click chemistry that has been creating a

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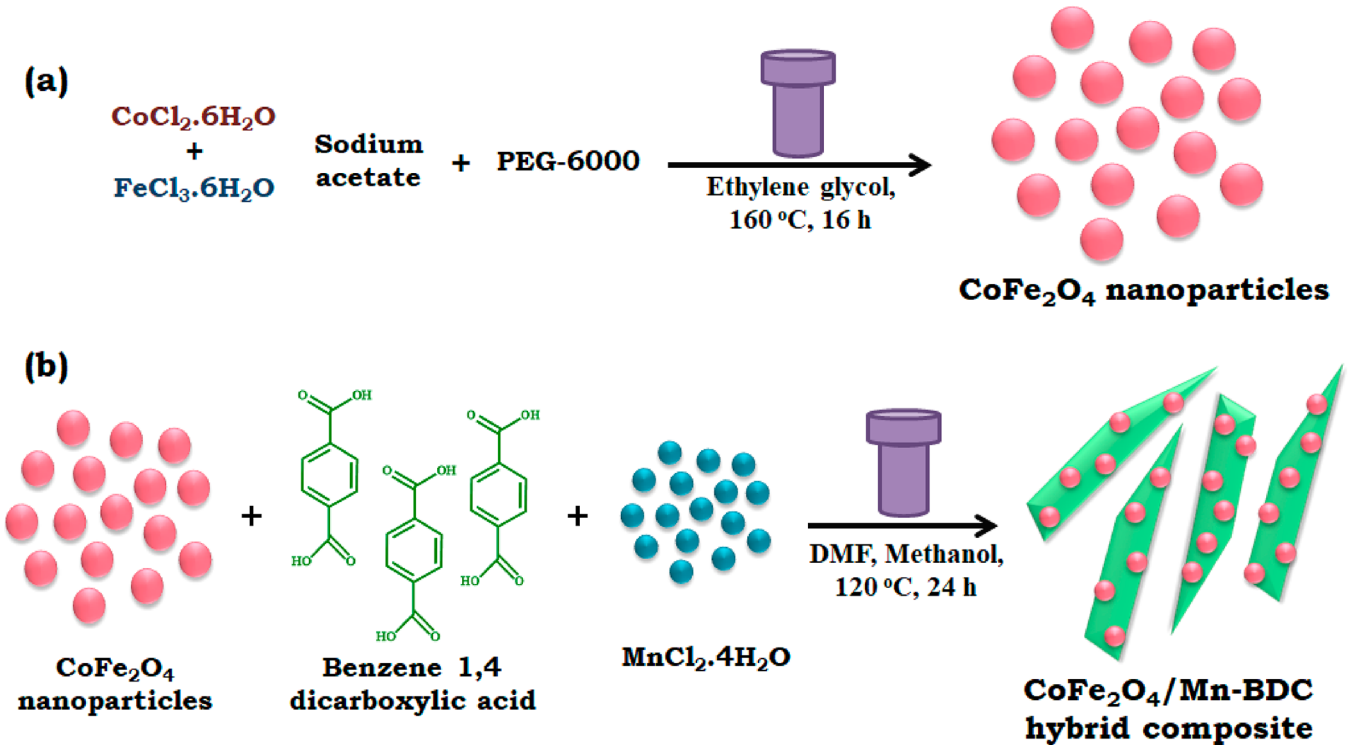
Scheme 1. Synthesis of $CoFe_2O_4$/Mn-BDC Hybrid Composite



renaissance in modern synthetic chemistry for the construction of ubiquitous carbon−heteroatom bonds.[32−35] Among various modular click approaches, Huisgen cycloaddition involving terminal alkynes and azides as substrates is the well-known synthetic route to furnish 1,2,3-triazoles with magnificent biological and therapeutic activities.[36−39] Even a few triazole derivatives, for example, cefatrizine, *tert*-butyldimethylsilylspiroaminooxathioledioxide, and Tazobactam, possess anticancer, antiviral, and antibiotic properties.[40−43] However, the premier cycloaddition route encountered serious drawbacks of difficult isolation and handling of toxic organic azides, which have prompted chemists and engineers to design other synthetic reaction pathways. Consequently, an alternative one pot strategy has been explored wherein in situ organic azide facilitates the access of entwined structures via click coupling among terminal alkynes, sodium azide, and alkyl/aryl halides.[44−52] Despite intensive efforts, none of the aforementioned methodologies have the potential to entirely address the formidable challenges often encountered in practical implications in pharmaceutical and medicinal industries. Severe limitations associated with these reported metal catalyzed transformations include harsh reaction conditions, a high temperature, low product yield, the use of additives, metal contamination, toxic solvents, catalyst reusability, leaching of active species, and many more. Therefore, the current status reveals the imperative need to explore new catalytic materials which can not only effectively deal with the aforesaid issues but also simultaneously meet the criteria of sustainability.

In our persistent research interests in exploring benign strategies for obtaining organic−inorganic composites and their exploitation as potent adsorbents and catalytic systems,[53−59] we hereby elucidate the fabrication of a hybrid $CoFe_2O_4$/Mn-BDC MOF composite endowed with superparamagnetic properties through a facile in situ solvothermal approach. The developed intricately designed material unveils magnificent catalytic performance in one-pot "click" coupling of terminal alkynes, aryl or alkyl halides, and sodium azide to obtain diverse triazole motifs with extraordinary pharmacological activities that can easily be metamorphosed into highly demanding drugs. Some of the striking aspects that render this expeditious synthetic protocol a potentially benign and sustainable option over already existing routes are ambient reaction conditions, a high turnover number, economic viability, an operationally simple procedure, an environmentally benign solvent, ease in scaleup, excellent yields, short reaction times, no use of additives, excellent durability, and effortless magnetic recovery of the catalyst. To the best of our insight, this is the first attempt to evaluate the catalytic efficacy of three-dimensional magnetic Mn-BDC MOF material in the concerned one-pot "click" reaction. In view of these considerations, we foresee that the current research work would not only enlighten the scientific community about the rational design of advanced MOF based architectures but also outline new directions in medicinal fields to access novel generic drugs in an eco-friendly manner.

EXPERIMENTAL SECTION

Materials and Reagents. Benzene 1,4 dicarboxylic acid (1,4-BDC) was procured from Tokyo Chemical Industry (TCI) Pvt. Ltd. Ferric chloride hexahydrate, cobalt chloride hexahydrate, and manganese chloride tetrahydrate were all obtained from Sisco Research Laboratories (SRL) Pvt. Ltd. The rest of the reagents and starting precursors were purchased from Spectrochem Private Limited.

Instrumentation. A PerkinElmer Spectrum 2000 was used to record Fourier transform infrared (FT-IR) plots of all the developed materials in the range of 4000−400 cm^{-1} using KBr. The size and shape of developed composites were determined through transmission electron microscopy (TEM) micrographs obtained from FEI TECHNAI G^2 T20 at 200 kV. In addition, scanning electron microscopy (SEM) images of synthesized materials were captured

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through a Jeol scanning electron microscope. Both compositional analysis as well as elemental mapping of fabricated composites was acquired from EDX equipment fitted with a SEM instrument. A Bruker D8 Advance instrument was employed to obtain powder X-ray diffraction data of designed materials in the 2θ range of 5−80° working at a scanning rate of 3° min^{-1}. For dispersion, developed nanoparticles were sonicated using a Tekmar Sonic Disruptor (model TM300). Flame atomic absorption spectroscopy was employed to calculate loading of the manganese in the final catalyst using N3180021 PinAAcle 500. Prepared nanoparticles and hybrid composites were subjected to vibrating sample magnetometry analysis wherein the magnetic field was varied from −10000 to 10000 Oe at room temperature (r.t.) via EV-9, Microsense, ADE. Successful synthesis of triazoles was affirmed using GC-MS analysis on an Agilent gas chromatogram (6850 GC) with a HP-5MS 5% phenylmethyl siloxane capillary column (30.0 m × 250 μm × 0.25 μm) and a quadrupole mass filter equipped with a 5975 mass selective detector (MSD) using helium as the carrier gas. A JEOL JNM-EXCP-400 instrument was used to record ^{1}H and ^{13}C NMR of obtained triazole derivatives.

Synthesis of Catalyst. *Preparation of $CoFe_2O_4$.* The developed magnetic MOF composite was synthesized in a stepwise manner, out of which the first step included the synthesis of $CoFe_2O_4$ using a solvothermal synthetic strategy.[60] In a typical procedure, 148.7 mg of $CoCl_2{\cdot}6H_2O$ and 337.9 mg of $FeCl_3{\cdot}6H_2O$ were dissolved homogeneously in 10 mL of ethylene glycol at 50 °C under magnetic stirring. Thereafter, sodium acetate (900 mg) and PEG-6000 (500 mg) were sequentially mixed into the above solution while stirring. After being continuously stirred for 30 min, the as obtained homogeneous mixture was subsequently transferred to an autoclave maintained at 160 °C for 16 h. The resulting black colored $CoFe_2O_4$ precipitate was isolated via an external magnet, which was further washed several times using double-deionized water and eventually dried at 60 °C for 6 h.

Preparation of Manganese Terephthalic Acid Metal Organic Framework (Mn-BDC). Mn-BDC was synthesized using a procedure reported by Shen and co-workers.[61] First of all, $MnCl_2{\cdot}4H_2O$ (0.76 g) and 1,4-BDC (0.83 g) were added to a round-bottom (R.B.) flask containing 40 mL of DMF and kept under magnetic stirring. This step was followed by the addition of 10 mL of methanol, and the resulting solution was kept under stirring for a further 10 min to obtain a homogeneous solution. The solution so obtained was transferred to an autoclave held at 120 °C for 24 h. The so formed solid powder was filtered, washed using methanol, and finally dried at 110 °C for 24 h in an oven.

Preparation of MOFs Decorated $CoFe_2O_4$ Nanoparticles ($CoFe_2O_4$/Mn-BDC). The $CoFe_2O_4$/Mn-BDC hybrid composite was synthesized using a facile procedure (Scheme 1). For this, $MnCl_2{\cdot}4H_2O$ (0.76 g) and 1,4-BDC (0.83 g) were added into an R.B. flask containing 40 mL of DMF under magnetic stirring to form a homogeneous solution. After this, 10 mL of methanol was added, and the resulting solution was stirred for another 10 min to obtain a homogeneous solution. After that, synthesized $CoFe_2O_4$ nanoparticles (0.4 g) were introduced into the above solution, and the overall assembly was then subjected to ultrasonication for 30 min. Eventually, the obtained solution was transferred to an autoclave and held at 120 °C for 24 h. Finally, the obtained composite was magnetically separated, washed using methanol, and dried at 110 °C for 24 h in an oven.

Procedure for $CoFe_2O_4$/Mn-BDC Mediated Synthesis of 1,4-Disubstituted 1,2,3-Triazoles. Terminal alkyne (1 mmol), sodium azide (1 mmol), aryl or alkyl halide (1 mmol), and $CoFe_2O_4$/Mn-BDC (25 mg) were added to an R.B. flask containing water (2 mL) and stirred at 50 °C for the appropriate time period. The reaction was simultaneously monitored via TLC, and once the reaction was completed, the obtained reaction mixture was allowed to cool to room temperature. Thereafter, the catalyst was magnetically separated followed by extraction of the reaction mixture with ethyl acetate and water; the so formed organic layer was dried using anhydrous sodium sulfate. Finally, GC-MS analysis of triazole products was carried out to authenticate their successful synthesis.

RESULTS AND DISCUSSION

The final catalyst was prepared as per Scheme 1. The first step involved in the fabrication of the overall composite is the synthesis of $CoFe_2O_4$ through a solvothermal preparation route. After that, the synthesized $CoFe_2O_4$ nanoparticles were added into the precursor salts of MOF to yield the $CoFe_2O_4$/Mn-BDC hybrid composite. The final catalyst was then subjected to a series of characterization techniques including SEM, FT-IR, TEM, EDX, ED-XRF, XRD, VSM, and AAS.

Catalyst Characterizations. In order to affirm the presence of a functional group in the fabricated materials, these samples were subjected to FT-IR analysis, and data were recorded in the range of 4000−400 cm^{-1}. Figure 1 represents

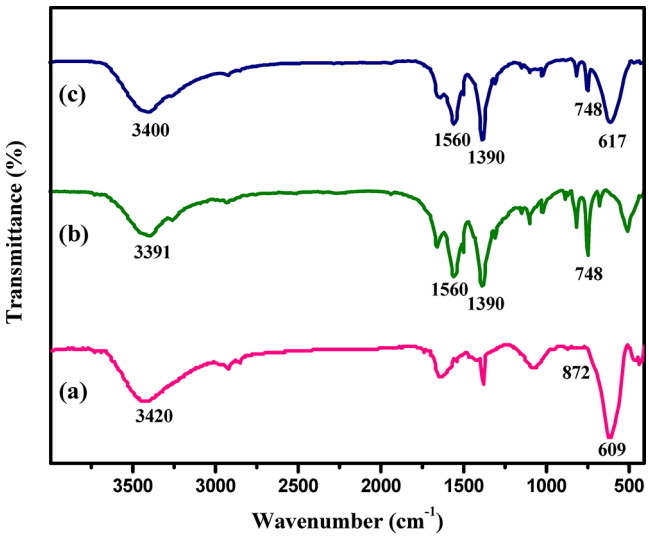

Figure 1. FTIR spectral plot of (a) $CoFe_2O_4$, (b) Mn-BDC, and (c) $CoFe_2O_4$/Mn-BDC.

FTIR spectra of $CoFe_2O_4$, Mn-BDC, and $CoFe_2O_4$/Mn-BDC. The $CoFe_2O_4$ spectrum reveals the presence of typical Fe−O and Co−O vibrations centered at around 609 and 872 cm^{-1}. In addition, the existence of surface hydroxyl (OH) groups on $CoFe_2O_4$ is confirmed by the presence of a broad band at around 3420 cm^{-1}.[60,62] Further, in the FTIR spectrum of Mn-BDC, the appearance of two peaks at 1390 and 1560 cm^{-1} corresponds to stretching vibrations (symmetric and asymmetric, respectively) in the organic ligands due to COO^{-} groups. In addition to this, the existence of a peak at 748 cm^{-1} clearly illustrates the effective coordination of manganese ions to 1,4-BDC. Furthermore, a comparison of the FTIR spectra of cobalt ferrite and the final catalyst successfully confirms the decoration of Mn-BDC MOF with inverse spinel $CoFe_2O_4$. The final catalyst spectra exhibit that bands at 1560, 1390, and 748 cm^{-1} are ascribed to the MOF, while the band around 617 cm^{-1} is due to the Fe−O vibrations of the $CoFe_2O_4$.

Knowledge of the structural integrity and crystallinity of developed hybrid composites was gained through XRD analysis (Figure 2) of $CoFe_2O_4$, Mn-BDC, and $CoFe_2O_4$/Mn-BDC. The $CoFe_2O_4$ XRD pattern reveals the presence of diffraction peaks at 2θ = 30.4°, 35.7°, 43.4°, 53.7°, 57.2°, and 62.7° which correspond to the (220), (311), (400), (422), (511), and (440) planes. The observed 2θ diffraction values

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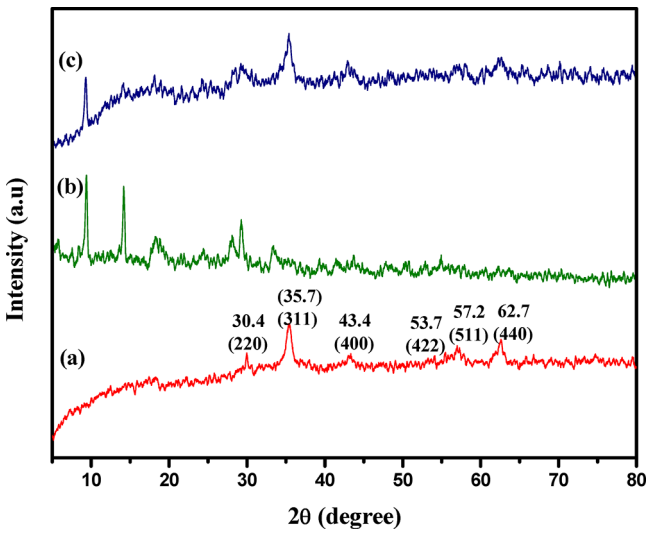

Figure 2. XRD spectral plot of (a) $CoFe_2O_4$, (b) Mn-BDC, and (c) $CoFe_2O_4$/Mn-BDC.

are in good agreement with the $CoFe_2O_4$ data in JCPDS (card number: 22-1086; Figure S1).[60] Additionally, in the XRD spectra of Mn-BDC, diffraction peaks at 9.4°, 14.2°, 18.8°, 19.3°, 24.4°, 28.2°, 29.4°, and 33.6° match with a simulated XRD plot generated utilizing previously reported single crystal X-ray data[63] and thus confirm the successful synthesis of the Mn-BDC framework (Figure S2). It is also evident from the PXRD spectra of Mn-BDC that it possesses a crystalline structure. Finally, the emerging peaks from the XRD spectrum of the $CoFe_2O_4$/Mn-BDC composite belong to both $CoFe_2O_4$ and Mn-BDC, suggesting the successful decoration of $CoFe_2O_4$ nanoparticles onto the Mn-BDC.

TEM and SEM are considered to be one of the highly powerful techniques that throw light not only on morphological features but also on the size of designed composites. TEM and SEM images of these hybrid materials have been provided in Figure 3. A TEM image of $CoFe_2O_4$ (Figure 3d) divulges the formation of spherical shaped nanoparticles having a diameter of approximately 200 nm. $CoFe_2O_4$ SEM analysis (Figure 3a) also discloses the fabrication of monodisperse nanoparticles with a spherical morphology. In addition, SEM and TEM images of bare Mn-BDC (Figure 3b and e) clearly show that the synthesized MOF has a homogeneous laminar microflake-like structure. Moreover, the SEM image of $CoFe_2O_4$/Mn-BDC (Figure 3c) shows the presence of dispersed magnetic inverse spinel cobalt ferrite nanoparticles on the surface of bare Mn-BDC, which further validates the successful preparation of the hybrid heterostructures.

EDX with elemental mapping was employed for the compositional analysis of the synthesized composites. Elemental mapping images of the hybrid $CoFe_2O_4$/Mn-BDC material reveals that it is composed of five elements, namely, Co, Fe, O, Mn, and C (Figure 4). On the basis of results obtained from elemental analysis, the loading of $CoFe_2O_4$ nanoparticles in the hybrid composite was found to be approximately 36% (Table S1). In addition, the EDX spectrum of $CoFe_2O_4$ shows distinct peaks of Co, Fe, and O, while the EDX spectrum of $CoFe_2O_4$/Mn-BDC indicates the appearance of well-defined peaks of Mn and C in addition to Co, Fe, and O, which further provides a concrete proof of the overall synthetic process (Figure 5). Moreover, ED-XRF of $CoFe_2O_4$/Mn-BDC also shows peaks of Mn, Co, and Fe further providing a vital clue for the synthesis of a hybrid heterostructure. In addition, quantitative estimation of the final hybrid catalytic system was carried out using the AAS

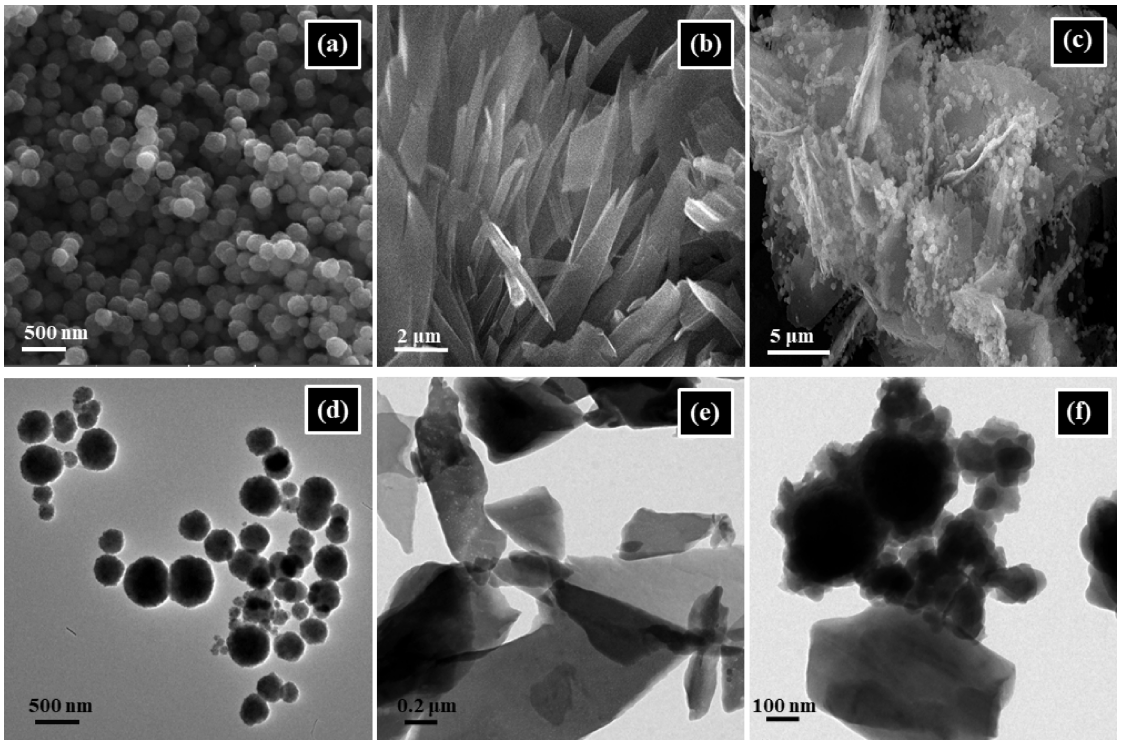

Figure 3. SEM micrographs of (a) $CoFe_2O_4$, (b) Mn-BDC, and (c) $CoFe_2O_4$/Mn-BDC and TEM micrographs of (d) $CoFe_2O_4$, (e) Mn-BDC, and (f) $CoFe_2O_4$/Mn-BDC.

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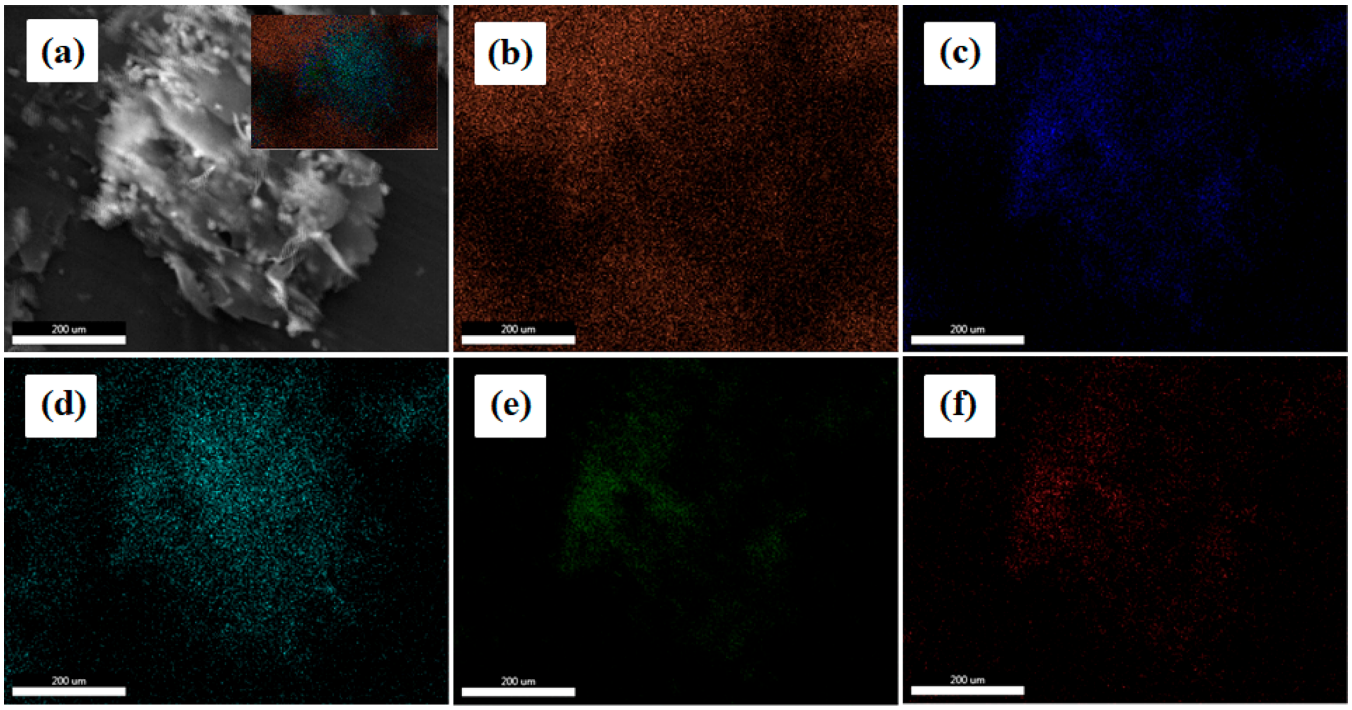

Figure 4. (a) SEM of $CoFe_2O_4$/Mn-BDC hybrid composite and the corresponding elemental mapping analysis of (b) C, (c) O, (d) Mn, (e) Fe, and (f) Co in the catalyst.

technique, which reveals that 0.499 mmol/g of manganese is present in $CoFe_2O_4$/Mn-BDC.

VSM analysis was employed to study magnetic properties of $CoFe_2O_4$, Mn-BDC, and $CoFe_2O_4$/Mn-BDC under a magnetic field varied from −10,000 to 10,000 Oe at r.t. (Figure 6). Further, superparamagnetic behavior of synthesized composites is confirmed by the magnetic hysteresis curves, exhibiting no obvious remanence and coercivity. In addition, it is found that the $CoFe_2O_4$ saturation magnetization (Ms) value is 57 emu/g, while Mn-BDC does not possess any magnetic character. However, upon integration with nonmagnetic Mn-BDC, a decrease in $CoFe_2O_4$ saturation magnetization is observed from 57 to 22 emu/g. Nevertheless, the saturation magnetization value of $CoFe_2O_4$/Mn-BDC is sufficient enough as it allows its complete, efficient, and rapid removal via an external magnetic force.

Activity of $CoFe_2O_4$/Mn-BDC in Click Coupling Reaction to Afford 1,4-Disubstituted 1,2,3-Triazoles. Catalytic competence of the newly fabricated $CoFe_2O_4$/Mn-BDC hybrid composite was explored in the multicomponent click protocol to access 1,4-disubstituted 1,2,3-triazoles. In addition, the effects of several thermodynamic and kinetic parameters including time, solvent, temperature, and amount of catalyst were studied for multicomponent click coupling.

In our preliminary reactivity tests, phenylacetylene and benzyl bromide were chosen as model substrates, and the results are compiled in Table 1. Initially the model reaction was performed in water at 50 °C for 2 h without a catalyst. However, the reaction failed to occur, further necessitating the need of a catalyst (entry 1, Table 1). After the addition of $CoFe_2O_4$/Mn-BDC into the same reaction system, 100% conversion percentage was detected after 2 h (entry 2). Additionally, $CoFe_2O_4$ nanoparticles also catalyzed the reaction with lower conversion percentage (entry 3). We further examined other solvents under the same conditions using $CoFe_2O_4$/Mn-BDC as the catalyst, but the results were not satisfactory (entries 4−6). The solvent screening studies indicate that water behaves as the best solvent for this reaction. Furthermore, reaction was carried out for discrete time periods, yet the results were very inferior (entries 7 and 8). Next, the variation in amount of catalyst in the concerned reaction was investigated (entry 9). As evident through GC-MS, conversion percentage was found to decrease on decreasing the amount of catalyst. Further assessment of the temperature conditions were carried out (entries 10 and 11). Both an increase and decrease in temperature resulted in lower conversion percentage. A variety of metal salts were further screened for their ability to stimulate the multicomponent click reaction. Adversely, the metal salts were totally ineffective in promoting the reaction (entries 12 and 13). Apart from this, the test reaction was also carried out with bare Mn-BDC, which also results in good conversion percentage (entry 14). Thus, the optimal reaction conditions were considered to include phenylacetylene (1 mmol), sodium azide (1 mmol), benzyl bromide (1 mmol), $CoFe_2O_4$/Mn-BDC (25 mg). and water as the solvent at 50 °C for 2 h.

Substrate Scope. In a quest to broaden the versatility of the designed hybrid composite, its catalytic efficiency has been assessed for a wide array of substituted phenylacetylenes and aryl halides under the optimized parameters (Table 2). Several features of this simple and inexpensive protocol are worth applauding. To our delight, when various terminal alkynes were subjected to the reaction under optimized conditions, triazole products were obtained with excellent conversion percentage. Next, the scope of a series of aryl halides was explored in the concerned reaction. The results revealed that the reaction also proceeded well with substituted benzyl chloride and benzyl bromide. The unsubstituted phenylacetylene gave 100% conversion percentage, while with the substituted phenylacetylenes, the conversion percentage

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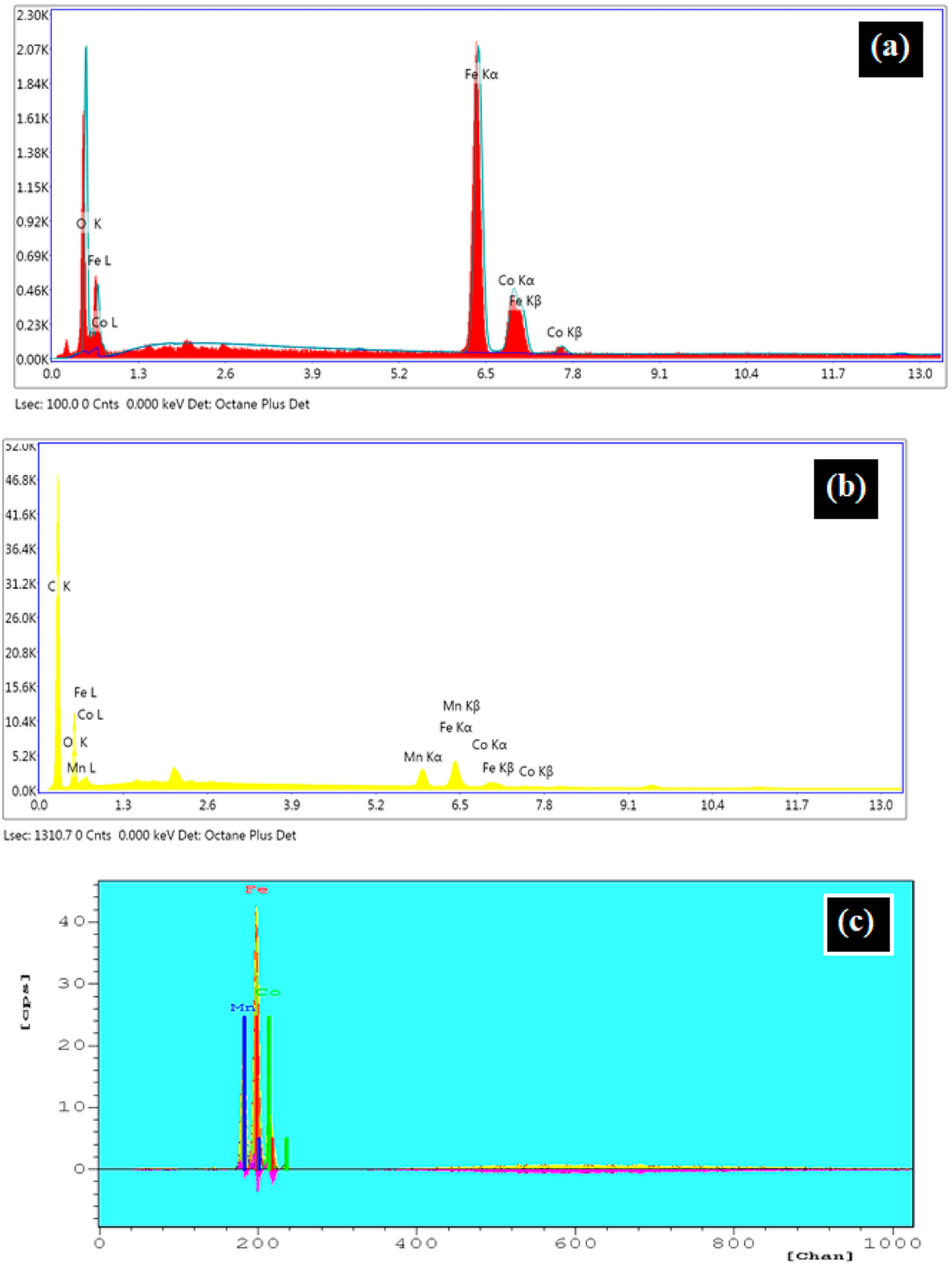

Figure 5. EDX of (a) $CoFe_2O_4$, (b) $CoFe_2O_4$/Mn-BDC, and (c) EDXRF of $CoFe_2O_4$/Mn-BDC hybrid composite.

decreased with the increasing electron donating capability of the substituents. This is evident from Table 2, entries 3, 8, and 10, which show that the conversion percentage is 96%, 24%, and 9% for 4-*tert* butyl phenylacetylene, 4-methyl phenylacetylene, and 4-methoxy phenylacetylene, respectively. Furthermore, the protocol was extended to aliphatic halides such as n-butyl bromide, which gave satisfactory results. Notably, the present click reaction not only exhibits wide substrate scope and high conversion percentage but also solely ends up in the formation of 1,4-disubstituted 1,2,3-triazoles.

Mechanistic Pathway. Scheme 2 illustrates a plausible mechanistic pathway for the concerned reaction using $CoFe_2O_4$/Mn-BDC as the catalyst. Initially, coordination between the magnetic Mn-BDC MOF based catalyst and the terminal alkyne forms a manganese coordinated acetylene complex (A), which is a better dienophile than acetylene itself. Simultaneously, alkyl halide upon in situ reaction with sodium azide results in the generation of an alkyl azide intermediate, which subsequently interacts with complex A to form complex B. This complex (B) further undergoes a 1,3-dipolar

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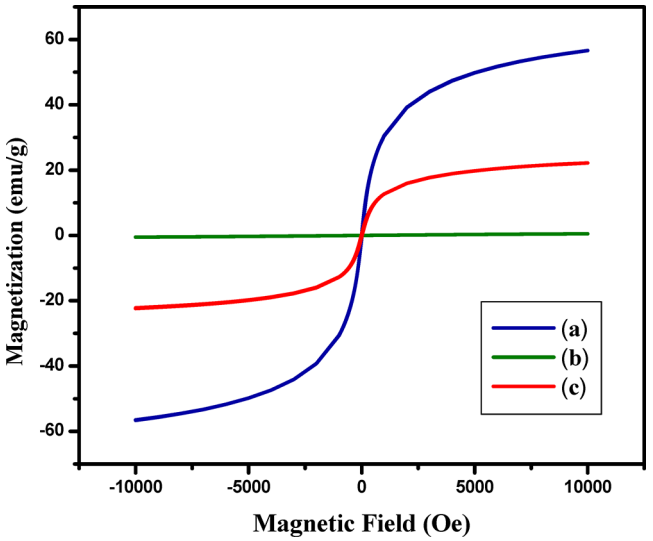


Figure 6. VSM of (a) $CoFe_2O_4$, (b) Mn-BDC, and (c) $CoFe_2O_4$/Mn-BDC hybrid composite.

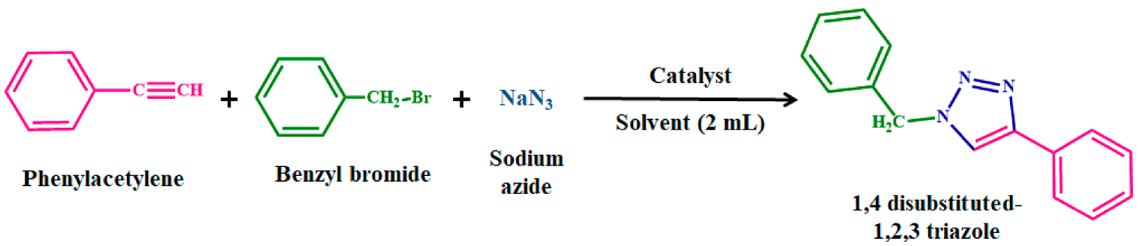
cycloaddition reaction to generate complex C. Finally, complex C affords the desired 1,2,3-triazole moieties (D) with the regeneration of $CoFe_2O_4$/Mn-BDC.

Heterogeneity and Recyclability Tests. With the aim of determining the intrinsic stability of the designed $CoFe_2O_4$/Mn-BDC hybrid catalyst, a standard heterogeneity test was conducted in which the test substrates (phenylacetylene and benzyl bromide) were again subjected to optimized reaction conditions. Thereafter, $CoFe_2O_4$/Mn-BDC was magnetically removed (after half the reaction time), while the reaction was further allowed to proceed for a prolonged duration. The absence of a leached catalytic metal center in the supernatant was confirmed through GC-MS. Once the $CoFe_2O_4$/Mn-BDC was taken out from the reaction media, there was no further increment in conversion percentage, which clearly debarred the probability of leached manganese metal from $CoFe_2O_4$/Mn-BDC.

Reusability and recyclability are the two most desired and indispensable parameters from an industrial and commercial perspective. Therefore, recyclability of the developed $CoFe_2O_4$/Mn-BDC hybrid catalyst was tested in the concerned reaction using phenylacetylene and benzyl bromide as representative substrates. Thereafter, $CoFe_2O_4$/Mn-BDC was retrieved under the influence of external magnetic forces upon the completion of the reaction, which was further washed with acetone and dried in an oven. Subsequently, the recovered $CoFe_2O_4$/Mn-BDC was utilized again in the same reaction as shown in Figure 7, which clearly signifies the retainment of its catalytic efficacy up to five consecutive runs. Further, the high stability of the designed hybrid catalytic system is evident from SEM, VSM, and XRD (Figures S3, S4, and S5, respectively) of recovered $CoFe_2O_4$/Mn-BDC, which reveals that its morphology, magnetization, and crystallinity remained unchanged after catalysis.

Comparison of $CoFe_2O_4$/Mn-BDC Activity with Reported Catalytic Materials. A critical comparison of the $CoFe_2O_4$/Mn-BDC catalyzed protocol was made with those already reported in the literature, and the results are presented in Table S2. A thorough analysis of reports related to the concerned reaction concludes that this is first ever MOF composite catalyzed synthetic route to afford 1,4-disubstituted 1,2,3-triazoles. Indeed, it is splendid to say that the developed catalyst displayed its supremacy over the literature precedents when compared on the basis of substrate scope, turnover number, catalyst retrievability, and optimized parameters like time, temperature, etc. In addition, $CoFe_2O_4$/Mn-BDC

Table 1. Optimization of the Reaction Parameters[a]



entry	catalyst	amount of catalyst (mg)	solvent (mL)	temp. (°C)	time (h)	conversion[b] (%)
1	no catalyst		water	50	2	
2	$CoFe_2O_4$/Mn-BDC	25	water	50	2	100
3	$CoFe_2O_4$	25	water	50	2	9
4	$CoFe_2O_4$/Mn-BDC	25	t-butanol	50	2	88
5	$CoFe_2O_4$/Mn-BDC	25	ethanol	50	2	20
6	$CoFe_2O_4$/Mn-BDC	25	acetonitrile	50	2	44
7	$CoFe_2O_4$/Mn-BDC	25	water	50	1	50
8	$CoFe_2O_4$/Mn-BDC	25	water	50	0.5	18
9	$CoFe_2O_4$/Mn-BDC	15	water	50	2	37
10	$CoFe_2O_4$/Mn-BDC	25	water	30	2	45
11	$CoFe_2O_4$/Mn-BDC	25	water	60	2	82
12	$CoCl_2 \cdot 6H_2O$	25	water	50	2	5
13	$FeCl_3 \cdot 6H_2O$	25	water	50	2	16
14	Mn-BDC	25	water	50	2	100

[a]Reaction conditions: Phenylacetylene (1 mmol), sodium azide (1 mmol), benzyl bromide (1 mmol), catalyst (x mg) and solvent (2 mL). [b]Conversion percentages were determined via GC-MS.

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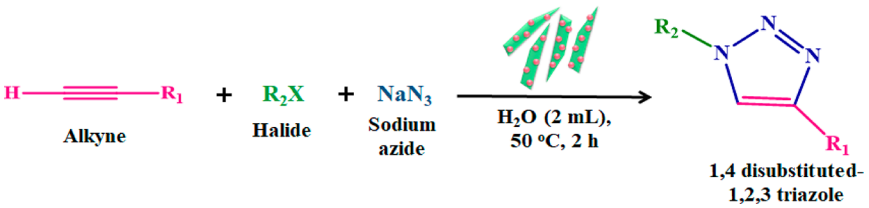
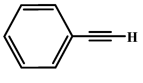
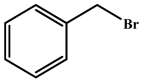
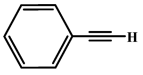
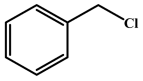
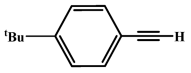
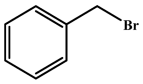
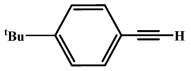
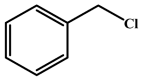
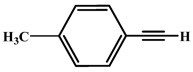
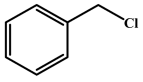
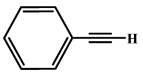
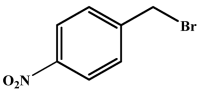
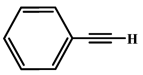
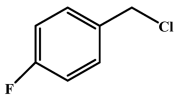
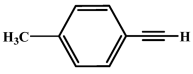
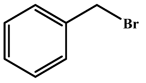
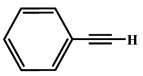
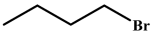
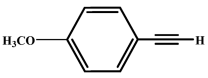
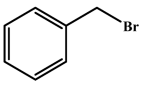
Table 2. Synthesis of 1,4-Disubstituted 1,2,3-Triazoles Using $CoFe_2O_4$/Mn-BDC[a]



Entry	Alkyne	Halide	Time (h)	Conversion[b] (%)	TON[c]
1.			2	100	801
2.			2	88	705
3.			2	96	793
4.			2	71	761
5.			2	25	200
6.			2	100	801
7.			2.5	68	545
8.			2	24	192
9.			2.5	31	248
10.			3	9	72

[a]Reaction conditions: Terminal alkyne (1 mmol), sodium azide (1 mmol), aryl/alkyl halide (1 mmol), $CoFe_2O_4$/Mn-BDC (25 mg), water (2 mL), 50 °C. [b]Conversion percentages were obtained from GC-MS. [c]TON represents no. of moles of obtained product per mole of catalyst.

retained its integral structure as well as catalytic potential even after five subsequent catalytic runs.

CONCLUSION

In conclusion, a magnetically retrievable Mn-BDC hybrid MOF catalyst has been fabricated using a solvothermal synthetic route and subsequently characterized with a multitude of advanced physicochemical tools including TEM, SEM, VSM, FTIR, XRD, EDX, ED-XRF, and AAS. Thereafter, catalytic performance of $CoFe_2O_4$/Mn-BDC is explored in click coupling to afford 1,4-disubstituted 1,2,3-triazoles. The adopted methodology being simple and operationally facile furnished several biologically and pharmaceutically significant molecules containing a triazole framework with satisfactory yield. On the basis of previous references pertaining to the concerned reaction, a tentative mechanism illustrating the role of the MOF based catalyst has been proposed. Furthermore, wider functional group tolerance, facile conditions, good

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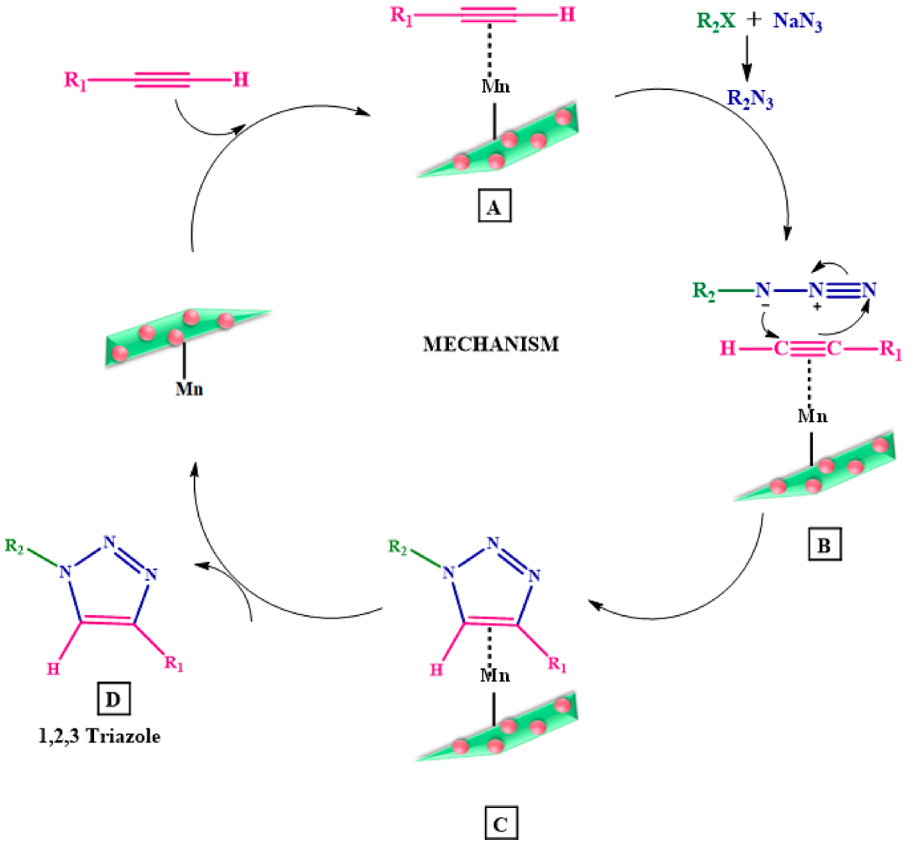
Scheme 2. Illustration of Plausible Mechanistic Route for the $CoFe_2O_4$/Mn-BDC Mediated Synthesis of 1,4 Disubstituted 1,2,3-Triazoles



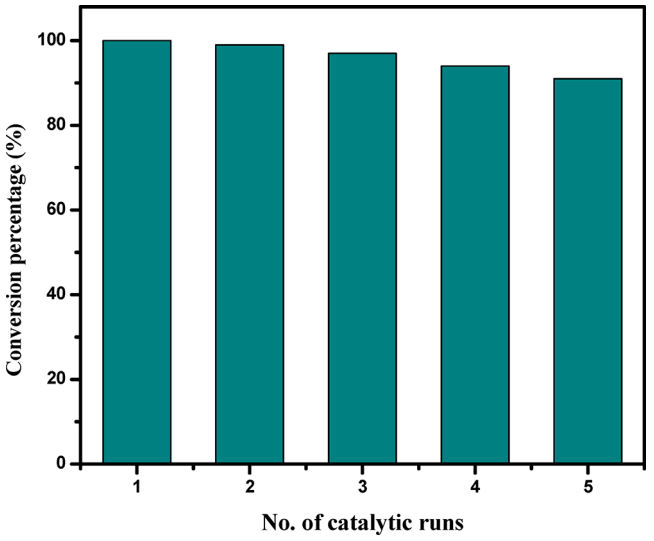


Figure 7. Recycling studies for the concerned reaction [reaction conditions: phenylacetylene (1 mmol), sodium azide (1 mmol), benzyl bromide (1 mmol), $CoFe_2O_4$/Mn-BDC (25 mg), water (2 mL), 50 °C, 2 h].

turnover number, and atom economy are some of the intriguing features of this protocol that make it economically compatible and competitive in comparison to those already reported in the literature. In addition, $CoFe_2O_4$/Mn-BDC in addition to facile retrievability through external magnetic forces can also be effectively reutilized for five subsequent catalytic runs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00752.

Comparison of $CoFe_2O_4$ PXRD with the database in JCPDS, Mn-BDC simulated XRD, characterizations (SEM, VSM, and XRD) of the recovered $CoFe_2O_4$/Mn-BDC, elemental mapping data of $CoFe_2O_4$/Mn-BDC, comparison of $CoFe_2O_4$/Mn-BDC catalytic activity, GC-MS spectra of the synthesized products, ^1H and ^{13}C NMR of obtained triazoles (PDF)

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Notes

The authors declare no competing financial interest.

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