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An efficient and sustainable catalytic reduction of carbon-carbon multiple bonds, aldehydes, and ketones using Cu nanoparticles decorated metal organic framework

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An efficient and sustainable catalytic reduction of carbon-carbon multiple bonds, aldehydes, and ketones using Cu nanoparticles decorated metal organic framework

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Cu nanoparticles decorated Cu-BTC-MOF is successfully demonstrated in the reduction of alkenes, alkynes, aldehydes, and ketones. The low cost, reusability, sustainability of the catalyst, the use of low amount of reducing agent, the eco-friendliness of the process, and the involvement of a simple work-up & separation of the products from the reaction system are some of the attractive key features.

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Abstract

Transition metal (Cu, Mn, Ni, Zr) substituted metal organic frameworks (MOFs) are prepared for the reduction of carbon-carbon multiple bonds with hydrazine hydrate in ethanol under a mild reaction condition. Among the MOFs investigated in this study, Cu framework substituted MOF exhibits the best activity in this study. Further, Cu nanoparticles (CuNPs) are supported on the surface of Cu framework substituted MOF to achieve the excellent reduction activity. The catalyst exhibits efficient recyclability with no appreciable loss in the catalytic activity even after five recycles. In order to establish the reaction mechanism, reactions are performed in N₂ and Ar atmosphere. Reaction is also performed in Ar atmosphere but in the presence of H_2O_2 to elucidate the mechanism. The catalyst exhibits excellent activity in the reduction of alkynes. Under the optimum reaction condition, catalyst is also successful in reducing a wide range of aldehydes and ketones. The present catalytic process demonstrates several key advantages such as a mild and convenient reaction condition, low substrate to hydrazine ratio, reusability, and cost-effectiveness of the catalyst (Pt or Pd free catalyst).

Keywords: Metal organic framework; Cu nanoparticles; reduction of carbon-carbon multiple bonds; reduction of aldehyde and ketone; heterogeneous catalyst.

1. Introduction

Reduction of olefins, alkynes, and carbonyl compounds is one of the important synthetic steps used in many catalytic and organic reactions.^{1,2} A wide range of hydrogen rich fuels and chemicals can be produced from the reduction of carbon-carbon multiple bonds.³ Further. reduction of aldehydes/ketones to alcohols produces a wide range of key fine chemicals and pharmaceuticals.⁴ Alcohols produced by the reduction of carbonyl compounds can act as solvents and precursors for the production of a wide variety of esters used in the flavour, fragrance, and cosmetic industries.^{5,6} Reduction of carbon-carbon multiple bonds are generally catalyzed by Pd, Ru, Rh, and Pt based costly catalysts and H₂ as an economical reducing agent.^{7,8} A wide range of metal complexes and metal nanoparticles based on costly metals have been investigated for the reduction of alkyne to alkene.^{9,10} Further, only a few reports are available for the complete reduction of alkyne to alkane.¹¹⁻¹⁴ Similarly, a wide range of homogenous and heterogeneous catalysts are known for the reduction of carbonyl compounds to alcohols by conventional reduction or transfer hydrogenation protocols.¹⁵⁻²³ Therefore, it is important for researchers to develop catalytic reduction methodology based on economical transition metals when compared to those costly scarce metals that are exclusively obtained as byproducts of major industrial metals.²⁴⁻³² Furthermore, for the reduction using transition metals based catalysts, different reducing agents such as, NaBH₄, hydrazine hydrate, formic acid etc can be used.^{33,34} Hydrazine is an economical and environmentally non eco-friendly chemical. Therefore, its consumption as a reducing agent will be advantageous and convenient for the hydrogenation in the production of fine chemicals. This would be one of the important methods to use surplus of the hydrazine produced worldwide. Efforts have been made to use hydrazine as a reducing agent with wide range of homogenous and metal nanoparticles supported catalysts.²⁷⁻³² The aim of this study is to develop robust and economical heterogeneous catalyst for the reduction of olefins, alkynes, and carbonyl compounds using hydrazine hydrate in base free condition.

A wide range of porous materials are known in the literature that includes zeolite, silica, metal oxide, carbon materials, and metal-organic-frameworks (MOFs). Metals and metal nanoparticles can be incorporated in these porous materials to develop various robust catalysts.³⁵⁻³⁹ Large external surface area, functional surface, and pore walls help to prevent the agglomeration of the NPs, thus resulting in narrow particle size and size distribution. Several strategies are known to prepare metal NPs, for example, (i) reduction of transition metal salt in the presence of porous support, (ii) chemical vapour deposition, (iii) photochemical reduction, (iv) ligand reduction and displacement from organometallics, and

(iv) electrochemical reduction method. Among these methods, the chemical reduction method is very straight forward and requires simple lab equipments to produce metal NPs. In this method, the reduction of corresponding metal salts is carried out in the presence of suitable reducing agent.

Among the porous materials discussed above, metal oxides and MOFs are interesting because metals are present in their framework structure. In these materials, support itself can act as a good catalyst. In the recent time, efforts are being made to develop catalysts based on MOF because they exhibit high surface area and porosity.⁴⁰⁻⁴² MOFs are being developed as a replacement of homogenous metal complexes but in the case of MOFs, only limited metal centres are accessible for the catalytic reactions. However, suitable metals and functional sites can be introduced in MOFs via in-situ synthesis and post-synthesis modification which makes them versatile catalysts.⁴³⁻⁴⁵ Efforts have been made to develop MOFs in the reduction of carbon-carbon multiple bonds. However, these MOF catalysts exhibited low activity (Significant amount of the catalyst was required for the reduction).²⁷ In the recent time efforts have also been made to develop metal NPs incorporated MOF (prepared using costly ligands & metal) for the reduction of styrene that involved additional base for the reduction to take place.⁴⁶ Ionic liquids mediated, PdNPs incorporated MOF has also been investigated for the selective reduction of alkynes.⁴⁷

The objective of this study is to develop an economical transition metal based ecofriendly and reusable catalyst for the reduction of carbon-carbon multiple bonds and carbonyl compounds. Another aim of this study is the base free and oxidant free reduction of carboncarbon multiple bonds using hydrazine hydrate as an economical and user-friendly reduction source. In this study, four different transition metal (Cu, Mn, Ni, Zr) substituted metal organic frameworks (MOFs) are investigated for the reduction of olefin. Among these MOFs, Cu based MOFs (Cu-BDC-MOF and Cu-BTC-MOF) exhibit better activity. Among the two Cu based MOF, Cu-BTC-MOF exhibits marginally higher activity. Therefore, Cu-BTC-MOF is investigated in details. Moreover, Cu-BTC-MOF is synthesized in eco-friendly water/ethanol medium whereas Cu-BDC-MOF needs to be synthesized in DMF medium. It is difficult synthesize Cu-BDC-MOF aqueous/ethanol medium. to in Further, Cu-BTC-MOF exhibits large surface area and pore volume which are some of the desired criteria for the catalyst to exhibit high catalytic activity. Catalytic activity of the best MOF found in this study is further improved by the incorporation of Cu nanoparticles (CuNPs) on its surface. CuNPs supported MOF is investigated in the reduction of wide range of olefins. Not only olefins but alkynes are also reduced using this protocol. The applicability of this protocol is also extended for the reduction of aliphatic and aromatic aldehydes and ketones.

2. Materials and Methods

2.1. Catalyst preparation

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Synthesis of Cu-BTC-MOF

Cu-BTC-MOF was synthesized by a solvothermal process.⁴⁸ First solution A was prepared by dissolving Cu(NO₃)₂·3H₂O (0.88 g) in 12 mL deionised water. Solution B was prepared by dissolving H₃BTC (benzene-1,3,5- tricarboxylate) (0.42 g) in 12 mL of ethanol. Solution A was added to solution B drop-wise in 30 minutes. Resultant solution was stirred at ambient temperature for 15 minutes. Finally, it was transferred into Teflon-lined stainless steel autoclave and hydrothermally treated at 110 °C for 18 h. After hydrothermal treatment, the autoclave was allowed to cool to ambient temperature. Solid precipitate was separated using centrifuge machine and the crystalline solid product was dried in vacuum oven at 80 °C for 10 h to get Cu-BTC-MOF (Cu₃(BTC)₂, molecular weight 604.87)⁴⁹.

Other MOFs such as Cu-BDC-MOF (Cu-BDC, molecular weight 300.76)⁴⁹, Zr-BDC-MOF (Zr₆O₄(OH)₄(BDC)₆, molecular weight 1628.034)⁴⁹, Mn-BDC-MOF (Mn₃(BDC)₃, molecular weight 663.69)⁴⁹, and Ni-BTC-MOF (Ni₃(BTC)₂, molecular weight 596.1)⁴⁹ were prepared by following the reported procedure.⁵⁰⁻⁵³ Details of their synthesis are provided in Supporting information section.

Synthesis of Cu(10%)/Cu-BTC-MOF

First CuNPs was synthesized. For the synthesis of CuNPs, Cu(NO₃)₂.3H₂O (0.19 g) was added to 50 mL of ethanol and stirred at 2-3 °C for 10 minutes to get solution A. Sodium dodecyl sulphate (0.31 g) and sodium borohydride (0.18 g) were dissolved in 35 mL of ethanol and stirred at 2-3 °C for 10 minutes to get solution B. Then the solution A was slowly added to solution B and the resultant solution was stirred at 2-3 °C for 30 minutes. Further, the solution was kept at ambient condition for 45 minutes. The resultant black solution confirmed the formation of CuNPs.

Cu-BTC-MOF (0.5 g) was dispersed in 15 mL of ethanol. The dispersed Cu-BTC-MOF was added to the colloidal CuNPs solution at ambient temperature. Resultant solution was kept for 5 h under stirring condition at ambient temperature. The resulting product was centrifuged, washed with ethanol, and dried in vacuum oven at 80 °C for 12 h.

2.2. Procedure of catalytic reduction

Substrate (0.6 mmol) was treated with N₂H₄.H₂O (1.2 mmol) in the presence of catalyst (20 mg) in ethanol (2 ml) for stipulated time period. Progress of the reaction was monitored using gas chromatograph (GC,Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 μ m). Product was confirmed using GC-MS (Schimadzu GCMS-QP 2010 Ultra Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 µm). Most of the reductions were initially carried out at ambient temperature (25-27 °C. However, in some cases, reactions were carried out at elevated temperature (80 °C or 120 °C) to achieve higher product yield. GC and MS spectra are provided for the reduction of styrene, phenylacetylene, and benzaldehyde in the supporting information section as examples after the GC-MS analysis (Fig. S1-S3).

3. Results and discussion

3.1. Physico-chemical characterization

Powder XRD was elucidated to confirm the formation of MOF materials. XRD pattern of Cu-BTC-MOF matches well with the XRD pattern reported for HKUST-1 (Fig. 1).⁴⁸ XRD patterns of Cu-BDC-MOF, Zr-BDC-MOF, Mn-BDC-MOF, and Ni-BTC-MOF match well with the XRD patterns of Cu-BDC, UiO-66, Mn-BDC, and Ni-BTC, respectively, reported in the literature (Fig. S4).⁵⁰⁻⁵³ Cu nanoparticles (CuNPs) were supported on the external surface of Cu-BTC-MOF. XRD pattern of Cu(10%)/Cu-BTC-MOF is similar to that of parent Cu-BTC-MOF (Fig. 1). However, the peak intensity in the diffraction pattern of Cu(10%)/Cu-BTC-MOF is significantly reduced (almost five times) when compared to the parent Cu-BTC-MOF. Distinguished reflection associated with CuNPs is not observed in the diffraction pattern of Cu(10%)/Cu-BTC-MOF which suggests that the sizes of CuNPs present on the external surface of Cu-BTC-MOF can be very small. Reduction in the peak intensity suggests that during the synthesis of CuNPs, partial destruction of framework structure has taken place. Intensity can also be reduced due to the partial occupation of the CuNPs on the exposed surface of Cu-BTC-MOF. With increase in loading of CuNPs, the intensity of XRD peaks decreases (Fig. S5). This result suggests that more concentration of $NaBH_4$ in the solution and more occupation of CuNPs on the exposed surface of Cu-BTC-MOF influence the XRD peak intensity.



Fig. 1. Powder XRD patterns of Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF.

N₂-adsorption experiments were carried out to determine the textural properties of the material. Cu-BTC-MOF exhibits a type II adsorption isotherm with gradual increase in the adsorbed volume in the range of 0.2 to 0.95 (P/P_0) followed by the steep adsorption with P/P_0 greater than 0.95 (Fig. 2). Changes in the isotherm behaviour are observed after the CuNPs loading. A somewhat reduced adsorption volume is observed in Cu(10%)/Cu-BTC-MOF. Changes in the isotherm behaviour suggest that the partial loss of surface coverage and porosity has taken place after the CuNPs loading. It is also possible that reducing environment influences the textural characteristics of the material. Micropore size distribution was determined from nonlocal density functional theory (NLDFT) and mesopore size distribution was determined from Barret-Joyner-Halenda (BJH) method. Micropore size distribution is similar for parent Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF materials (Fig. 2, inset b). It shows micropores in the range of 0.5 to 0.9 nm. A difference in the mesopore size distribution is observed. Cu-BTC-MOF shows mesopore size distribution in the range of 3-5 nm with peak maximum at 3.8 nm whereas Cu(10%)/Cu-BTC-MOF shows bi-modal mesopore size distribution in the range of 1.5-7 nm with peak maxima at 1.9 nm and 2.9 nm (Fig. 2, inset a). Table 1 clearly shows that the loading of CuNPs reduces the surface area and pore volume of the material. Cu-BDC-MOF, Mn-BDC-MOF, and Ni-BTC-MOF exhibit type

II isotherms similar to that of Cu-BTC-MOF but much less adsorbed volume (Fig. S6a). Multi-modal pore size distribution is observed for these three samples (Fig. S6a, inset). Surface area and pore volume of these samples are significantly lower than Cu-BTC-MOF (Table S1). Zr-BDC-MOF exhibits type IV isotherm with H2 hysteresis loop (Fig. S6b). A gradual increase in the N₂-adsoption is observed in the range of 0.2 to 0.6 (P/P₀) which is followed by a steep adsorption above P/P₀ of 0.7. Adsorption above P/P₀ = 0.7 corresponds to capillary condensation in the mesopores. Bi-modal mesopore size distribution for Zr-BDC-MOF are lower than Cu-BTC-MOF but significantly higher than other MOFs investigated in this study (Table 1 and Table S1).



Fig. 2. N₂-adsorption desorption isotherms of Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF. Inset shows (a) BJH pore size distribution and (b) NLDFT pore size distribution.

	^a Surface area	External surface	Total pore	Cu content
Entry	$S_{BET} (m^2/g)$	area (m ² /g)	volume (cc/g)	(Wt %) ^b
Cu-BTC-MOF	932	298	1.01	17.8
Cu(10%)/Cu-BTC-MOF	758	240	0.84	26.2
^c Cu(10%)/Cu-BTC-MOF	749	232	0.82	26.0

Table 1. Physico-chemical properties of various catalysts investigated in this study.

^aS_{BET} calculated from the adsorption branch in the region of $0.05 < P/P_0 \le 0.3$.^bObtained from MP-AES.^cTextural properties of the recovered catalyst after the recycling process.

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Fig. 3. SEM images of (a-c) Cu-BTC-MOF and (d-f) Cu(10%)/Cu-BTC-MOF.

Morphology of the materials was investigated using SEM (Fig. 3). Small magnification SEM image shows that Cu-BTC-MOF crystals are of varied morphology such as octahedral, triangular, and distorted octahedral and so on (Fig. 3a-c). One high magnification image of octahedral crystal is shown in Figure 3c. The surface of this crystal is very smooth. Morphology of Cu(10%)/Cu-BTC-MOF crystals is somewhat distorted when it is compared with the morphology of the parent Cu-BTC-MOF as shown in the small

magnification SEM image (Fig. 3d-f). One such distorted octahedral image is presented here (Fig. 3f). High magnification SEM image shows that surface of the crystal is rough which suggests that the external surface was corroded when it was in the direct contact with the solution containing NaBH₄ and SDS (Fig. 3f). NaBH₄ reducing environment seems to affect the outer morphology of the parent material while CuNPs are supported on its surface. Cu-BDC-MOF and Mn-BDC-MOF shows aggregated crystal morphology with different dimensions (Fig. S7). Zr-BDC-MOF shows aggregated flake like crystal morphology (Fig. S7). The details of micro-nano structure of the highly active catalyst Cu(10%)/Cu-BTC-MOF were investigated using high resolution transmission electron microscope (HRTEM). Cu-BTC-MOF and CuNPs domains are clearly visible in the TEM images (Fig. 4a,b). HRTEM images also reveal that CuNPs are present in the sample (Fig. 4c,d). HR-TEM image further confirms the loading of 3-7 nm CuNPs on the surface of Cu-BTC-MOF (Fig. 4e). Lattice fringes with interlayer spacing of 1.8 nm confirm the formation of CuNPs (Fig. 4f).



Fig. 4. TEM images of Cu(10%)/Cu-BTC-MOF.



Fig. 5. Thermograms of Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF.

Thermogravimetric analysis shows different weight loss profiles for both these materials (Fig. 5). Cu-BTC-MOF shows the weight loss in the range of 30-135 °C due to the removal of physisorbed H₂O molecules present in the porous structure. Somewhat stable profile is obtained in the range of 135-340 °C. Loss occurred in this temperate range is due to the removal of ethanol molecules present in the micropores. A sharp decrease in the weight loss at 350 °C is due to the framework decomposition of Cu-BTC-MOF. Only a marginal decrease in the weight loss is observed in the range of 400-1000 °C confirming the stability of copper oxide formed after the decomposition of Cu-BTC-MOF. TGA profile shows that 18.2% of CuO is remained after 1000 °C heating. Cu(10%)/Cu-BTC-MOF shows the weight

loss in the range of 30-135 °C due to the removal of physisorbed H₂O molecules present in matrix. Further, a stable profile is observed in the range of 135-300 °C. Loss occurred in this temperate range is due to the removal of ethanol molecules present in the micropores. A sloping decrease in the weight loss in the range of 300 – 600 °C is due to the framework decomposition of Cu-BTC-MOF and the removal of any occluded SDS. Only a marginal decrease in the weight loss is observed in the range of 600-1000 °C confirming the stability of copper oxide and Cu present in Cu(10%)/Cu-BTC-MOF. TGA profile shows that 26.8 wt% of CuO and CuNPs in the sample. Based on these results, it can be concluded that 8.6% of CuNPs is loaded in the sample. Thermograms of various other MOFs synthesized in this study are provided in Figure S8. Different compositional behaviour and stability are clearly observed from the thermograms of various MOFs investigated in this study.

The FT-IR spectrum of Cu-BTC-MOF shows characteristic absorptions at 1645 cm⁻¹ and 1371 cm⁻¹ which are attributed to asymmetric stretching frequency and symmetric stretching frequency of deprotonated carboxylic group. This suggests the coordination of Cu⁺² with carboxylate group of BTC ligand (Fig. S9a). The ring-out-of-plane vibration of the linker BTC molecules appeared at 729 cm⁻¹, which further suggests the effective coordination of the Cu ions to the BTC ligands. The peak at 490 cm⁻¹ can be assigned to Cu-O stretching vibration. FT-IR spectrum of Cu(10%)/Cu-BTC-MOF is very similar to that of Cu-BTC-MOF, except some marginal shift in the peak position (Fig. S9a). The broadening of peak at 490 cm⁻¹ confirms the incorporation of different types of Cu species (Cu-O and Cu metal) in the sample. The characteristic bands of the carboxylate group located at 1660-1510 cm⁻¹ (asymmetric vibration) and 1470-1390 cm⁻¹ (symmetric vibration) are observed for various MOFs investigated in this study (Fig. S9b). These bands suggest the coordination of metal ions with the deprotonated carboxylate group of the linker (BTC/BDC). Less intense bands located around 1100 cm⁻¹ and in the range of 860-710 cm⁻¹ indicate stretching vibrations of C-C groups and the in-plane & the out-of-plane deformation vibrations of the C-H groups in the benzene ring of BTC and BDC ligands. FT-IR peaks in the range of 400-650 cm⁻¹ confirm the formation of M-O in the MOF structure (Fig. S9b).

DRUV-visible spectroscopy provides indirect evidence for the incorporation of Cu in the MOF framework structure and CuNPs on the external surface of MOF (Fig. S10). Charge transfer bands are observed in the range of 250-450 nm whereas absorption above 600 nm is associated with d-d transition.⁵⁴ In addition, absorption in the range of 500-600 nm is attributed to the plasmonic resonance of Cu_n nanoparticles. Cu-BTC-MOF exhibits charge

transfer absorption in the range of 200-310 nm and 350-450 nm. In addition, absorption in the range of 500-1000 nm with a peak maximum of 700 is observed (Fig. S10a). Cu(10%)/Cu-BTC-MOF exhibits almost similar absorption in the range of 200-500 nm. However, some change in the absorption band in the range of 500-1000 nm is observed, which confirms the incorporation of CuNPs/CuO species in the matrix of Cu-BTC-MOF. Shift in the absorption spectrum in the range of 500-600 nm further suggests the formation of CuNPs/CuO species. DRUV–vis spectra of Zr-BDC-MOF, Mn-BDC-MOF, Cu-BDC-MOF and Ni-BTC-MOF exhibit absorptions in the range of 250–450 nm which are attributed to the metal to ligand and ligand to metal charge transfer bands (Fig. S10b). In addition, absorption in the range of 500-1000 nm corresponds to d-d transition.



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Fig. 6. High resolution XPS spectrum for Cu species present in Cu(10%)/Cu-BTC-MOF.

The details of various Cu species present in Cu(10%)/Cu-BTC-MOF were obtained from XPS investigation. High resolution XPS spectrum obtained for Cu species is presented in Figure 6. Two spin-orbit peaks in the Cu 2p spectrum are observed which are consistent with the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ electronic configurations. Deconvolution of Cu $2p_{3/2}$ shows that it has peaks at about 932.2 and 934.2 eV, for Cu⁰/Cu⁺ and Cu²⁺ species, respectively.⁵⁵ Shake up satellite peak at 943.4 is observed due to Cu²⁺ species. XPS analysis results are consistent with the results obtained from DRUV-visible investigation. Bulk chemical composition was determined using elemental analysis (Table 1). Analysis shows that 17.8 wt% of Cu is present in Cu-BTC-MOF. After the CuNPs incorporation, Cu content is increased to 26.2 wt %, which signifies that amount of CuNPs loading is 8.4 wt % (Table 1). Amount of CuNPs loading in Cu(5%)/Cu-BTC-MOF and Cu(15%)/Cu-BTC-MOF were estimated to be 4.6 wt% and 13.1 wt%, respectively.

3.2. Catalytic activity

The objective of this study was to develop economical transition metal based robust catalyst for the reduction of various compounds. Reaction condition was optimized using highly active catalyst. First, it was important to find suitable active catalyst for this transformation. Styrene was chosen as a model reactant to screen the catalytic activity of various MOFs prepared in this study (Table 2). Cu-BTC-MOF exhibited the highest activity among various MOFs investigated in this study (Table 2). The activity of Cu-BDC-MOF was only marginally lower than Cu-BTC-MOF (Table 2). CuNPs were supported on the Cu-BTC-MOF. With increase in the loading of CuNPs from 5 wt% to 10 wt%, the ethylbenzene yield was increased from 74.2 wt% to 96.4 wt% (Table 2). However, with further increase in the CuNPs loading from 10 wt% to 15 wt%, ethylbenzene yield was decreased from 96.4 to 86.9 % (Table 2). These optimizations lead us to conclude that 10 wt% CuNPs loading was optimum to achieve the highest yield. Based on the results obtained, it can be concluded that an optimum loading of CuNPs (10 wt%) in the catalyst could provide highly dispersed CuNPs sites which were accessible and reactive during the reduction of styrene.

Table 2. Influence of various MOF catalysts investigated in the reduction of styrene.



Entry No.	MOF (Amount in mmol)	Ethyl benzene	TON
		yield (%)	
1.	Zr-BDC-MOF (0.0122)	15.6	7.6
2.	Mn-BDC-MOF (0.0301)	24.2	4.8
3.	Cu-BDC-MOF (0.0664)	61.1	5.5
4.	Cu-BTC-MOF (0.0330)	66.3	12
5.	Ni-BTC-MOF (0.0335)	22.2	4
7.	Cu(10%)@Cu-BTC-MOF (0.0358)	96.4	16.2
8.	Cu(5%)@Cu-BTC-MOF (0.0355)	74.2	12.6
9.	Cu(15%)@Cu-BTC-MOF (0.0360)	86.9	14.5
^a 10.	Cu(10%)@Cu-BDC-MOF (0.0358)	91.3	15.3

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Reaction condition: Styrene (0.6 mmol), N₂H₄.H₂O (1.2 mmol), ethanol (2.0 mL), temperature (RT, 25-27 °C), time (6 h). ^aCatalytic activity data after 5th recycle.

Influence of catalyst amount was investigated by varying the catalyst amount in the range of 5 mg to 25 mg (Table S2). 20 mg of the catalyst was required to achieve the better activity when catalyst amount and product yield both were considered. Having found the best catalyst for the selective reduction of styrene to ethylbenzene, influence of reaction medium was investigated (Table S2). Various polar and nonpolar solvents were investigated. Reaction

took place in various medium but ethylbenzene yield was significantly varied by varying the reaction medium. Non polar solvents were less effective than polar solvents (Table S2). Reaction proceeded well in polar protic solvent ethanol. However, it was not preceded well in the water medium. Further, the reaction also took place in the neat condition but the yield of ethylbenzene was very low (Table S2). Therefore, ethanol was chosen as an optimum reaction medium for further investigation. Several reducing agents/transfer hydrogenation reagents such as isopropanol, formaldehyde, formic acid, and NH₃ were employed but all of them were found ineffective in the reduction process (Table S2).

Cu(10%)/Cu-BTC-MOF was easily recovered using centrifuge machine and reused for five times. Recycling study showed that no significant decrease in the ethylbenzene yield was observed (Fig. S11). Elemental analysis of the recovered catalyst showed that 0.13 wt% of Cu was leached to the solution after five recycles. After the fifth cycle, the recovered catalyst was subjected to XRD and other physico-chemical characterization. XRD pattern (Fig. S12), SEM image (Fig. S13), and FT-IR spectrum (Fig. S14) of the recovered catalyst were similar to that of fresh catalyst. Surface area of the recovered catalyst was similar to that of the fresh catalyst (Table 1). To confirm that the reaction took place due to the heterogeneous catalyst and not due to the leached Cu in the solution, catalyst was removed from the reaction mixture after 1.5 h and the reaction was continued further for 4.5 h. The plot of ethylbenzene yield and reaction time confirmed that the reaction did not proceed further after the removal of catalyst (Fig. S15). Analysis of the reaction mixture solution showed that only 0.05 wt% Cu was leached to the reaction mixture that was unable to catalyze the reaction under this experimental condition.

Reduction using hydrazine is believed to be mediated through diimide (the hydrogenating source. Diimide are produced in-situ in the presence of H_2O_2 or air.⁵⁶⁻⁵⁷ In this study, Cu(10%)/Cu-BTC-MOF produces diimide via dissolved O₂ present in the reaction mixture, and transfers hydrogen to styrene resulting in the formation of ethylbenzene. To prove this hypothesis, three control experiments were performed. Reactions were carried out in N₂ and Ar atmosphere. Before the reaction, reaction flask was de-aerated and the flask was maintained under N₂/Ar atmosphere before adding hydrazine. After 6 h of reaction only 6.7 and 4.9 % ethylbenzene yields were obtained in N₂ and Ar atmosphere, respectively. These experiments support the assumption that diimide is acting as a reagent in the reduction of styrene (Scheme 1). Similarly, one more reaction was conducted. In this reaction, the flask was de-aerated and then it was put under Ar atmosphere. After that H_2O_2 (two times excess to that of hydrazine) was added after the addition of hydrazine. In this case 68.9 % ethylbenzene

yield was obtained. These control reactions confirmed that oxygen was responsible for the diimide formation which plays key role in the reduction process. Based on the catalytic results obtained using Cu(10%)/Cu-BTC-MOF, and the model reactions, a reaction mechanism is proposed (Scheme 1). Two catalytically active sites are present in Cu(10%)/Cu-BTC-MOF, one is the framework Cu and the other is the CuNPs. Both these sites simultaneously activate the hydrazine and the in-situ generated hydrazine adducts produce diimide which reduce the olefin via the concerted or double coordination mode²⁷ to produce the alkane (Scheme 1). Cu-BTC-MOF exhibited large surface area with average pore diameter of 3.8 nm. Therefore, the active sites present on the internal surface and on the external surface were easily accessible for the reactant molecules in the reduction process. However, CuNPs sizes were in the range of 3-7 nm that could only be present on the external surface of the Cu-BTC-MOF. Therefore, in the case of Cu(10%)/Cu-BTC-MOF the reduction due to CuNPs took place on the external surface but the reduction due to Cu present in the Cu-BTC-MOF could take place on the internal surface as well as on the external surface. In one of the early literature, it is reported that Cu ion is the best among the wide range of metal ions investigated that include Sb, As, Bi, Cr, Ce, Co, Au, Fe, Pb, Mg, Hg, Mo, Ni, Os, Pd, Pt, Ag, Te, Sn, and V for the activation of hydrazine in the reduction reaction.⁵⁸ The catalytic hydrogenation is mediated through the activation of hydrazine hydrate to diimide followed by the H_2 generation for the reduction reaction which is facilitated efficiently by the Cu-BTC-MOF/Cu-BDC-MOF investigated in this study.



Scheme 1: Mechanism for the reduction of alkene, alkynes, aldehydes, and ketones using CuNPs decorated Cu-BTC-MOF using hydrazine hydrate as reducing agent.

A range of styrene derivatives were reduced to corresponding ethylbenzene derivatives in excellent yield at the ambient temperature (Table 3). Substituted styrene, for example, α -methyl styrene was converted to cumene. However, the yield was somewhat lower than ethylbenzene (in case of styrene) under identical condition (Table 3, compare entries 1 and 5). Similarly, aliphatic olefin such as 1-octene was reduced to octane in good yield at ambient temperature (Table 3, entry 6). However, reduction had to perform at the elevated temperature (80 °C) to obtain the good yield of cyclohexane in the reduction of cyclohexene (Table 3, entry 7). Similarly, α -substituted styrene such as cinnammylalcohol/cinnamic acid was reduced at the elevated temperature (80 °C) to get the moderate to excellent yield (Table 3, entries 8-9). Comparative catalytic activity data reported in literature for the reduction of styrene to ethylbenzene over various heterogeneous catalysts using hydrazine hydrate as reducing agent are presented in (Table S3).^{27, 59-61} Comparative data shows that Cu(10%)/Cu-BTC-MOF exhibits better or comparable activity with other heterogeneous catalysts reported in the literature.

Entry	Substrate	Temp. (°C)	Product yield (%)	TON
1		25		16.2
2	H ₃ C	25	(96.4) H_3C	15.5
3	H ₃ CO	25	(92.1) H ₃ CO	13.9
4	ci	25		15.2
5		25	(90.6)	12.9
6		25	(76.6)	13.2
7		80	(78.4)	13.3
8	CH ₂ OH	80	(79.2) ————————————————————————————————————	12.6
9	СООН	80	(75) СООН	15.1
			(90)	

Table 3. Reduction of olefins using Cu(10%)/Cu-BTC-MOF.

Reaction condition: Substrate (0.6 mmol), $N_2H_4.H_2O$ (1.2 mmol), ethanol (2 mL), catalyst (0.0358 mmol, 20 mg), time (6 h). (RT = 25-27 °C)

Having accomplished the reduction of a wide range of olefins, the interest was to extend the application of this catalyst in the complete reduction of alkynes. Under the optimum condition, applicable for styrene reduction, phenylacetylene was observed to get reduced only to a small extent, wherein styrene was obtained in high selectivity (Table 4, entry 1). When the same reaction was conducted at a higher hydrazine to phenylacetylene ratio (4:1) at ambient temperature, the conversion was not improved much but the selectivity towards ethylbenzene was improved (Table 4, entry 2). The conversion of phenylacetylene and selectivity for ethylbenzene were significantly improved when the reaction was carried

out at elevated temperature of 80 °C and hydrazine to phenylacetylene ratio of (4:1) (Table 4, entry 3). These reactions provided evidence that the increase in reaction temperature and phenylacetylene to hydrazine hydrate ratio (1:4), excellent conversion and ethylbenzene selectivity were achieved. Substituted phenylacetylene derivatives also exhibited impressive activity under the optimized reaction condition (80 °C, 6 h) (Table 4, entries 4 and 5). However, diphenylacetylene was difficult to reduce. In this case, only E-stilbene was obtained as a selective product at 80 °C. When the temperature of the reaction was increased to 120 °C, diphenylacetylene conversion slightly improved but E-stilbene was obtained as a selective product. Due to the strained ring and hindered rotation, diimide was difficult to bind in the vicinity of diphenylacetylene for providing H_2 to the substrate and therefore low reactivity was obtained. Aliphatic compounds such as 1-octyne was converted to octane with more than 90% selectivity, however it required longer duration (12 h) and higher reaction temperature (120 °C) when compared to the phenylacetylene. Recycling study showed that no significant decrease in the ethylbenzene yield was observed after five recycles during the reduction of phenylacetylene (Table 4, entry 12). XRD pattern (Fig. S12) and FT-IR spectrum (Fig. S14) of the recovered catalyst were similar to that of fresh catalyst. Comparative data shows that Cu(10%)/Cu-BTC-MOF exhibited better or comparable activity with other heterogeneous catalysts reported in the literature (Table S4).^{11-14, 21}

S.N	Alkyne	Temp. (°C)	Time (h)	Alkyne conv. (%) (TON)	Product s	elect. (%)
1 ^a		25	6	14.4 (2.4)	(94.6)	
2		25	6	18.6 (3.1)		
3		80 °C	6	96.8 (16.3)	(55.8)	(44.2)

Table 4. Reduction of alkynes using Cu(10%)/Cu-BTC-MOF.

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Reaction condition: Alkyne (0.6 mmol), N_2H_4 . H_2O (2.4 mmol), ethanol (2 mL), catalyst (0.0358 mmol, 20 mg). (RT, 25-27° C). ^a N_2H_4 . H_2O (1.2 mmol). ^bCatalytic activity data after five cycle.

Having got success in the reduction of olefins and alkynes, our interest was to examine whether the same protocol can be extended to the reduction of C=O also. Reduction of aldehyde and ketone to corresponding alcohol is an important organic transformation. Similar to styrene, benzaldehyde was also completely reduced to benzylalcohol at ambient

temperature in 6 h under the same reaction condition (Table 5). Though substituted benzaldeyde was also reduced at ambient temperature, but good yield was obtained at elevated temperature (80 °C). Various aliphatic and aromatic aldehydes were converted to alcohols in good yields at 80 °C (Table 5). Similarly, aliphatic and aromatic ketones were converted to corresponding alcohols in moderate to good yields at 80 °C (Table 5). The reduction of aldehyde was more facile when compared to the ketone. Cinamaldehyde was reduced under the same reaction condition but at 120 °C. Complete conversion of cinamaldehyde was observed but the selectivity towards cinamylalcohol was only 18 %. Progress is underway to develop selective catalyst based on MOF which can selectively reduce cinamaldehyde to cinamylalcohol in high yield. Recycling study showed that no decrease in the benzylalcohol yield was observed after five recycles during the reduction of benzaldehyde (Table 5, entry 13). XRD pattern (Fig. S12) and FT-IR spectrum (Fig. S14) of the recovered catalyst were similar to that of fresh catalyst. Comparative data shows that Cu(10%)/Cu-BTC-MOF exhibited better or comparable activity with other heterogeneous catalysts reported in the literature (Table S5).^{15, 17-23}

Entry	Substrate	Time (h)	Temp. (°C)	Product yield (%)	TON
1	СНО	6	25	CH₂OH	16.8
2	сі—————————————————————————————————————	6	25	(100) СІ—СН ₂ ОН	8.1
3	СІ—————————————————————————————————————	6	80	$CI \longrightarrow CH_2OH$	14.9
4	СНО	6	25	(65) OH	7.6
5	СНО	6	80	(43) OH	14.1
6	СНО	12	120	(84) CH ₂ OH	3.0
7		6	25	(18) ————————————————————————————————————	6.0
8		6	80	(36) ————————————————————————————————————	10.9
9	O	6	25	(45) OH	7.6
10	o	6	80	OH	13.1
11	⊘⊨o	6	25	(78)	5.4
12	o	6	80	(32)	11.3
13 ^a	СНО	6	25	(67) — СН ₂ ОН	16.8
				(100)	

Table 5. Reduction	of aldehydes and I	ketones using Cu	(10%)/Cu-BTC-MOF.
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Reaction condition: Substrate (0.6 mmol), N₂H₄.H₂O (1.2 mmol), ethanol (2 mL), catalyst (0.0358, 20 mg), (RT, 25-27 °C). ^a Catalytic activity data after five cycle.

4. Conclusions

Transition metal (Cu, Zr, Mn, Ni) containing metal organic frameworks were investigated in the reduction of olefins using hydrazine hydrate as a reducing agent under the mild reaction condition. Among the MOFs investigated in this study, Cu-BTC-MOF exhibited the highest activity in the reduction of styrene. Further CuNPs decorated Cu-BTC-MOF was successfully prepared and thoroughly characterized. CuNPs(10%)/Cu-BTC-MOF exhibited better activity than the parent Cu-BTC-MOF. Loading of CuNPs on the surface of Cu-BTC-MOF provided CuNPs and Cu₂O isolated active sites that enabled higher activity than the parent Cu-BTC-MOF. The Cu (10%)/Cu-BTC-MOF exhibited efficient recyclability even after five recycles. Leaching experiments showed that extremely low quantity of Cu was leached during the reaction and the Cu present in the catalyst catalyzed this reaction in the heterogeneous manner. CuNPs(10%)/Cu-BTC-MOF was unable to reduce the styrene in N_2/Ar environment in the presence of hydrazine hydrate. However, they were able to reduce styrene and produced good yield of ethylbenzene in the presence of H_2O_2 and hydrazine hydrate in Ar environment. These investigations confirmed that air or O_2 are required to catalyze this reduction process. Based on these investigations, catalytic data, and physicochemical characterizations, reaction mechanism for the reduction using hydrazine hydrate was proposed. The reduction protocol was successful in the reduction of a wide range of aliphatic and aromatic olefins. The highly active catalyst exhibited excellent activity in the reduction of a wide range of aliphatic and aromatic alkynes. Finally, the application of the highly active CuNPs(10%)/Cu-BTC-MOF is successfully demonstrated in the reduction of aldehydes and ketones. Following are the key advantages of the present protocol: (i) the reusability and sustainability of the catalyst, (ii) the use of low amount of reducing agent, (iii) the eco-friendliness of the process (because N_2 is the by-product of this reduction process), (iv) the involvement of a simple work-up and separation of the products from the reaction system. The progress is underway to develop a unique catalyst which can reduce difficult alkene and alkynes.

Associated content

Supplementary Information

The Supporting Information is available free of charge on the RSC Publications website at DOI: . Supporting information includes details of materials, catalyst preparation, catalyst characterization. Figures S1-S15 include GC-MS analysis data, XRD patterns, N₂-adsorption desorption isotherms, SEM images, thermograms, FT-IR spectra, DRUV-visible spectra, recyclability and leaching studies plots, XRD, FT-IR and SEM of recycled catalyst. Table S1-S5 includes textural properties of MOFs, influence of catalyst amount, various solvents & reducing agents, comparative catalytic activity data reported in the literature for the reduction of styrene, phenylacetylene, and benzaldehyde.

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