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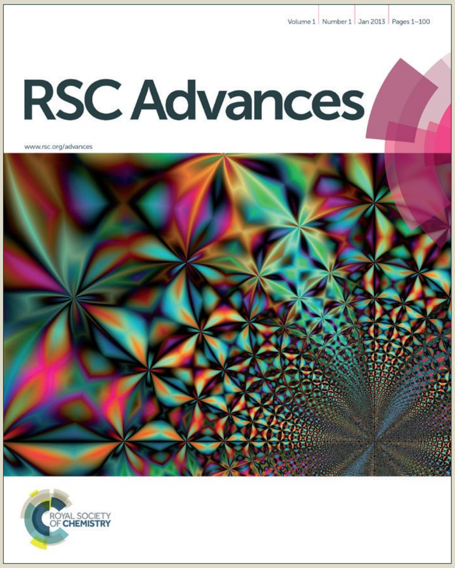

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Cu ion-exchanged and Cu nanoparticles decorated mesoporous ZSM-5 catalysts for the activation and utilization of phenylacetylene in the sustainable chemical synthesis

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Abstract

Mesoporous ZSM-5 was synthesized using 1,4-diazabicyclo[2.2.2]octane based multi-cationic surfactant as structure directing agent. Cu^{2+} exchanged mesoporous ZSM-5 was prepared by the ion-exchange process. Cu nanoparticles decorated mesoporous ZSM-5 was prepared using $NaBH_4$ as reducing agent. Materials were characterized by the complementary combination of X-ray diffraction, N_2-adsorption, UV-visible, and scanning/transmission electron microscopic techniques. For comparative purpose, Cu^{2+} exchanged ZSM-5, HY, and NaY; and Cu nanoparticles decorated conventional ZSM-5, SBA-15, and Al_2O_3 samples were also prepared. Sustainable catalytic process was developed for the selective synthesis of indolizine, chalcone, and triazole derivatives using mesoporous ZSM-5 based heterogeneous catalyst. Multi-component synthetic strategy is reported here for the selective synthesis of above mentioned chemicals that involves phenylacetylene as one of the building blocks. Control experiments were performed to ascertain the proposed reaction pathways. Recycling and leaching experiments were performed to demonstrate the sustainability and robustness of the catalytic process. Among these catalysts, Cu nanoparticles decorated mesoporous ZSM-5 exhibited the highest activity in all these reactions. Catalyst was found to be highly stable and it was possible to recycle the catalyst five times with no appreciable loss in the activity. A wide range of indolizine, chalcone, and 1,2,3-triazole derivatives were prepared in high yields using this catalyst.

Keywords: Cu nanoparticles; Mesoporous zeolite; Multi-component reactions; Regioselectieve synthesis, Green and sustainable synthetic process.

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1. Introduction

Microporous zeolites play significant role in the sustainable development of catalytic process for the synthesis of bulk and fine chemicals involving small molecules.[1] These syntheses are accomplished due to the tuneable acidity of zeolites. Acidity of zeolites can be finely tuned by varying the Si/Al ratio or by the post-synthesis treatment.[2] That is the reason zeolites play crucial role in the petrochemical industry.[3] It is possible to synthesize zeolites having tuneable pore size with wide range of Si/Al ratio.[2] Furthermore, by varying the Si/Al ratio, zeolites with different framework structure can be synthesized.[2] ZSM-5 zeolite rules the petrochemical industry due to its shape selectivity whereas zeolite Beta rules the fine chemical industry due to its large pore diameter.[3] Though microporous zeolites impart good activity in many catalytic transformations, however, their role is limited in several applications due to the following reasons: (1) large molecular organic transformations are restricted due to small micropore size, (2) applications are mostly based on acid catalyzed reactions, (3) only a few transition metals can be incorporated in the zeolite framework structure that limit their wide applications in several important organic transformations. In the recent time, significant efforts are being made for the development of hierarchical/nanocrystalline zeolites with inter/intra-connected microporous-mesoporous structure.[4] We have contributed in this area and developed a wide range of structure directing agents for the synthesis of mesoporous zeolites.[5] These materials exhibited excellent activity in the acid catalyzed reactions involving large organic molecules.[6] The difficulty to incorporate transition metals in the zeolite matrix can be taken care up to some extent by the incorporation of metals as metal ions through ion-exchange process or by supporting metal/metal oxide nanoparticles on the zeolite surface. Due to the recent development of mesoporous zeolites now it is possible to support highly dispersed metal/metal oxide nanoparticles on the large external surface of nanocrystalline zeolites.[7]

Metal nanoparticles are known to exhibit excellent activity in several important organic transformations.[8] Metal nanoparticles are stabilized by organic molecules known as capping agent to restrict their aggregation in aqueous or non-aqueous medium. However, it is difficult to separate and reuse them. Efforts have been made to prepare metal nanoparticles supported on the surface of heterogeneous catalysts such as metal oxides, silica, zeolite, carbon, etc., for the efficient recovery and reuse.[9] In general, Au, Ag, Ru, Pt, Pd and other costly metal nanoparticles are found to exhibit good to excellent activity in the organic transformations useful to fine and pharmaceutical industry.[10] Efforts are being made to design

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and develop economical catalysts based on transition metals. Cu is an interesting metal that can exhibit surprising activity in several organic transformations.[11]In the recent years, efforts are being made to investigate organic reactions using Cu based catalysts that are generally catalyzed by Au, Ag or Ru based catalysts.[12] In general, high surface area materials are required to support metal nanoparticles. In addition to this, surface functional groups are important in stabilizing metal nanoparticles on the surface. Due to less external surface area and less number of surface silanol groups, it is difficult to prepare highly dispersed metal nanoparticles on the surface of conventional zeolites. Development of mesoporous zeolites opens up wide opportunity to use them as suitable heterogeneous catalyst and good support materials in bulkier molecular transformations.

In this manuscript, mesoporous ZSM-5 (hereafter written as Meso-ZSM-5) with nanosheet morphology was prepared. Cu^{2+} ion-exchanged Meso-ZSM-5 and Cu nanoparticles supported Meso-ZSM-5 catalysts were prepared and investigated in the green chemical synthesis of chalcones, indolizines and 1,2,3-triazoles. One-pot, multi-component synthesis strategy was adopted to prepare these pharmaceutically important synthetic intermediates. For comparative purpose, Cu^{2+} exchanged ZSM-5, HY, and NaY; and Cu nanoparticles decorated conventional ZSM-5, mesoporous silica SBA-15, and Al_2O_3 samples were also investigated.

2. Experimental

2.1. Materials

All chemicals were of AR grade and used as received without further purification. Ludox (Hs-40, 40 % aqueous solution), tetrapropylammonium bromide (TPABr), SiO_2, Al_2O_3, and organic substrates used in the catalytic reactions were purchased from Sigma Aldrich, India. Sodium borohydride ($NaBH_4$) was obtained from Spectrochem Pvt. Ltd., India. Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and Aluminum sulfate ($Al_2(SO_4)_3$. $18H_2O$) were obtained from Loba Chemie Pvt. Ltd., India. Sodium dodecyl sulfate was obtained from SD Fine Chemical Ltd., India. Solvent used in this study were procured from Merck India Pvt. Ltd. HY and NaY were kindly provided by SÜD Chemie India Pvt. Ltd.

2.2. Catalysts synthesis

For the synthesis of Meso-ZSM-5, first structure directing agent (C_{18}-[D-C_6]$_3$-D-C_{18}) was prepared by following the reported procedure.[5d] Meso-ZSM-5 was synthesized in the

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basic condition (pH ≈ 12) using multi-quaternary ammonium C_{18}-[D-C_6]$_3$-D-C_{18} as structure directing agent (SDA) by following the molar composition of 6.67 Na_2O: 0.75 Al_2O_3: 30 SiO_2: 1.5 C_{18}-[D-C_6]$_3$-D-C_{18}: 2132 H_2O. In a typical synthesis, sodium silicate (Si/Na=2.25, 12.25 wt% SiO_2 in aqueous sodium silicate solution) (14.7 g), aluminium sulphate (0.50), C_{18}-[D-C_6]$_3$-D-C_{18} (2.76 g), and distilled water (25.5 g) were mixed to obtain the above mentioned gel composition. The resultant reaction mixture was vigorously stirred using magnetic stirrer at ambient condition for 10 h. Finally, the reaction mixture was transferred to a Teflon-coated stainless-steel autoclave and hydrothermally treated at 423 K for 6 days under static condition. After the reaction, the product was filtered, washed with distilled water, and dried at 383 K. Solid product was calcined at 823 K for 6 h under flowing air in order to remove the organic SDA.

Conventional ZSM-5 was synthesized by following the reported procedure using tetrapropylammonium bromide as structure directing agent.[13] CuO was prepared by following the reported procedure.[14] For comparative study, mesoporous silica SBA-15 was also prepared. The details of synthesis and textural properties of SBA-15 are provided in supporting information (Fig. S4, Table S1).

In this study, Cu^{2+} ion-exchanged and Cu nanoparticles supported zeolite materials were prepared. 2 g of calcined zeolite was added to 50 mL of 1M $CuCl_2$ aqueous solution and the reaction mixture was stirred at 343 K for 6 h. After 6 h, solid was filtered, washed with deionized water, and dried at 373 K for 12 h. This process was carried out three times. Cu^{2+} ion-exchanged conventional ZSM-5 and Meso-ZSM-5 are represented as Cu-ZSM-5 and Cu-Meso-ZSM-5, respectively.

Cu nanoparticles supported zeolites were prepared by chemical reduction method by following the reported procedure.[7c] In this study, 5 wt % and 10 wt % of Cu nanoparticles supported zeolites were prepared. Detail for the synthesis of 10 wt% Cu nanoparticles supported on zeolite is given as an example. First, solution A was prepared by the dissolution of 380 mg of Cu $(NO_3)_2.3H_2O$ in 150 mL of deionized water, which was kept in ice for 10 minutes. Another solution B was prepared by the dissolution of 620 mg SDS (sodium dodecyl sulphate) and $NaBH_4$ (500 mg) in 250 ml of deionized water, which was also kept in ice for 10 min. Solution A was added drop-wise into solution B for 30 minutes at ice cold condition under stirring condition. Resultant solution was stirred for additional 30 minutes under ice-cold condition. After this, stirring was stopped and the resulting mixture was kept at ambient temperature under static condition for 45 minutes. Meanwhile, 1 g support material was dispersed in 50 ml deionized water using ultrasonic bath for 15 min. Finally,

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well dispersed zeolite suspension was added in one proportion to the above nanoparticles solution and kept for 5 h at ambient temperature under stirring condition. After 5 h, resulting mixture was centrifuged and washed several times with ethanol, followed by deionized water to remove the surfactant. Finally, the solid obtained was dried in vacuum at 353 K for 12 h. Cu nanoparticles supported on ZSM-5 and Meso-ZSM-5 samples are designated as Cu(x%)/ZSM-5 and Cu(x%)/Meso-ZSM-5, respectively, where x = 5 or 10. Cu(10%)/SBA-15 and Cu(10%)/Al_2O_3 were also prepared by following the above mentioned procedure.

2.3. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–60° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA) and a proportional counter detector. Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at 573 K for 3 h in the degas port of the adsorption apparatus. The specific surface area of the material was calculated from the adsorption data points obtained at P/P_0 between 0.05–0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using Barrett-Joyner-Halenda (BJH) and NLDFT methods. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology of the zeolites. For deeper understanding structural analysis were carried out using a FEI, TF30-ST transmission electron microscope (TEM) operating at 300 kV equipped with a scanning unit and a high-angle annular dark field (HAADF) detector from Fischione (model 3000). The compositional analysis was performed using energy dispersive X-ray (EDX, EDAX Inc.) spectroscopy attachment on the TF30. Sample was dispersed in ethanol using ultrasonic bath, and dispersed sample was mounted on a carbon coated Cu grid, dried, and used for TEM measurement. DRUV-visible spectra were recorded by Shimadzu (UV-2600) spectrophotometer.

2.4. Procedure of catalytic reactions

2.4.1. Synthesis of chalcones and indolizines

10 ml round bottom flask was charged with 2-pyridinecarboxaldehyde (1.0 mmol), piperidine (1.0 mmol), phenylacetylene (1.0 mmol), dichloromethane (DCM, 4 mL) and catalyst (40 mg). Then the reaction flask was fitted with a condenser and magnetically stirred in a temperature-controlled oil bath at 343 K for 3 h under N_2 atmosphere. After 3 h, catalyst

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was removed by centrifugation and the reaction mixture was monitored by gas chromatograph (GC) (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 μm). Product was confirmed using GC–MS (Schimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

For the synthesis of chalcone, the reaction was performed in neat condition (in the absence of solvent) by following the above synthesis procedure for 9 h.

2.4.2. Synthesis of 1,2,3-triazoles from epoxides/benzyl halides

In a typical synthesis, epoxides or benzyl halides (2.0 mmol), sodium azide (2.0 mmol), phenylacetylene (2.0 mmol), water (4 mL), and catalyst (40 mg) were charged into a 10 mL round bottom flask. Then the reaction flask was fitted with a condenser and magnetically stirred in a temperature-controlled oil bath at 343 K for 6 h under N_2 atmosphere. After 6 h, reaction mixture was centrifuged and the reaction mixture was extracted with ethyl acetate. Products were isolated with column chromatography using 100-200 mesh silica gel and hexane/ethyl acetate mixture as eluent. Products were confirmed using ^{1}H and ^{13}C NMR that matched well with the reported NMR data.

3. Results and discussion

3.1. Physico-chemical characterization

Meso-ZSM-5 exhibits XRD pattern corresponding to a highly crystalline MFI framework structure with high phase purity (Fig. 1a). Cu(10%)/Meso-ZSM-5 clearly shows the diffraction peaks corresponding to both Cu nanoparticles (hereafter represented as CuNPs) and Meso-ZSM-5 phases. Three additional diffraction peaks located at 2θ; 43.1, 50.3, and 73.9° are observed in Cu(10%)/Meso-ZSM-5 when compared with Meso-ZSM-5, which can be assigned to (111), (200), and (220) planes of CuNPs (Fig. 1a).[15] The XRD pattern of Cu(5%)/Meso-ZSM-5 exhibits weak diffraction peaks corresponding to CuNPs because of low Cu content in Cu(5%)/Meso-ZSM-5. Cu(10%)/ZSM-5 also exhibits well resolved diffraction peaks corresponding to both CuNPs and ZSM-5 phases (Figure not shown). The textural properties of the zeolite material were investigated using nitrogen adsorption-desorption measurements. Meso-ZSM-5 exhibits type-IV isotherm similar to that of mesoporous materials (Fig. 1b). A sharp increase in the volume of N_2 adsorption in the region $0.4<P/P_0<0.95$ is characteristic of capillary condensation in the inter/intra-crystalline

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mesopore void spaces present in the Meso-ZSM-5. Both micropores and mesopores contribute to the porosity (total pore volume) of the material. The difference in the total pore

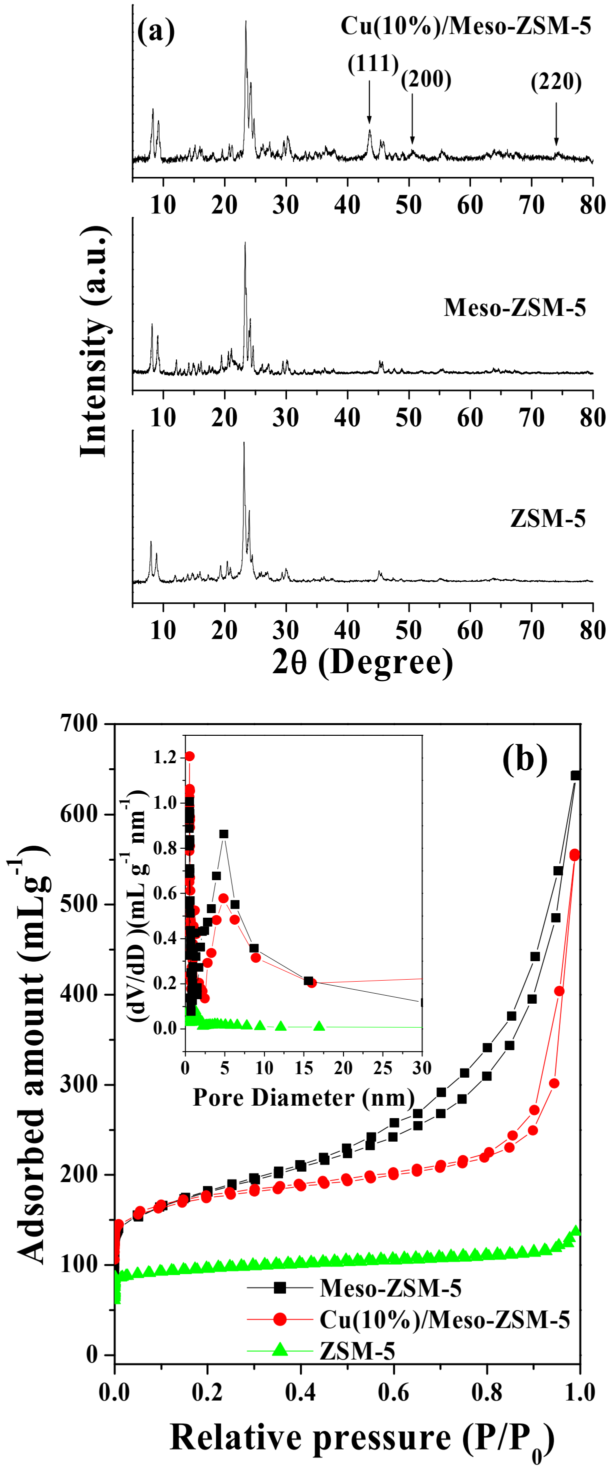

Fig. 1. (a) XRD patterns and (b) N_2-adsorption desorption isotherms (inset shows pore size distribution) of ZSM-5, Meso-ZSM-5, and Cu(10%)/Meso-ZSM-5.

volume of ZSM-5 and Meso-ZSM-5 materials is due to the mesoporosity present in Meso-ZSM-5. Mesopores in Meso-ZSM-5 are formed due to the void space between the nearest neighbouring nanosheets. Pore size distribution indicates that the nanosheets maintain local coherence but assembles in somewhat disordered manner that lead to form widely distributed pore size (Fig. 1b, inset). Textural properties of zeolite materials investigated in this study are summarized in Table 1. The N_2-adsorption study confirms that the surface area and total pore volume decreased after the incorporation of CuNPs on its surface (Table 1). Meso-ZSM-5 has large external surface area with large number of surface silanol groups that makes it an ideal support for the decoration of metal nanoparticles.

Table 1. Physico-chemical properties of ZSM-5 materials investigated in this study.

Entry	[a]Surface area S_{BET} (m^2/g)	External surface area (m^2/g)	Mesopore volume (cc/g)	Total pore volume (cc/g)	[b]Cu content (%)
ZSM-5	302	71	0.08	0.20	-
Cu-ZSM-5	297	69	0.08	0.20	6.13
Meso-ZSM-5	600	215	0.83	1.02	-
Cu-Meso-ZSM-5	-	-	-	-	6.52
Cu(5%)/Meso-ZSM-5	-	-	-	-	4.34
Cu(10%)/Meso-ZSM-5	543	195	0.76	0.97	8.45
Cu(10%)/ Meso-ZSM-5[c]	526	186	0.73	0.95	8.40
Cu(10%)/ZSM-5	249	64	0.07	0.19	7.38

[a]S_{BET} calculated from the adsorption branch in the region of $0.05<P/P_0\leq0.3$. [b]Obtained by ICP analysis. [c]Textural properties of the recovered catalyst after the recycling catalyst.

Large micrometer size ZSM-5 particles are observed in the SEM micrograph. Similar morphology is observed for CuNPs supported ZSM-5 (Fig. 2). Oval shaped flower like zeolite crystals are observed in the SEM micrograph of Meso-ZSM-5 that are built with nanosheet like flower petals (Fig. 2). Cu(10%)/Meso-ZSM-5 also exhibits the similar morphology to that of Meso-ZSM-5 which confirms that $NaBH_4$ reduction procedure for the synthesis of CuNPs did not disturb the morphology of parent materials (Fig. 2). Details of

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micro-nano structure is provided here for the highly active CuNPs(10%)/Meso-ZSM-5 and Meso-ZSM-5 which was obtained from TEM investigation. TEM images confirm the oval like morphology of Meso-ZSM-5 particles in the nanocomposite material (Fig. 3). Some irregular zeolite particles can also be seen in the TEM images (Fig. 3). High resolution TEM (HRTEM) image shows that oval or irregular shape particles are built with nanosheet like crystal morphology (Fig. 3). TEM also reveals that zeolite growth has taken place in one direction and these uni-directional grown zeolite nanosheets self-assembled to form oval shape nanoarchitecture. Selected area diffraction pattern indicates that material is highly ordered in the micropores length scale (Fig. 3e, inset). Further examination of HRTEM images reveals that CuNPs are adhered to the surface of zeolite nanosheets. Highly dispersed, well defined spherical CuNPs of the dimension of 2-3 nm can be seen in the HRTEM images of CuNPs(10%)/Meso-ZSM-5 (Figs. 3g, h). HRTEM image also shows lattice fringes, which further confirms the highly crystalline nature of the material (Fig. S1a, ESI). To confirm the presence of Si, Al, O, and Cu elements in the material, EDX analysis was performed. EDX spectrum (Fig. S1b, ESI) clearly shows the incorporation of CuNPs on the surface of Meso-ZSM-5.

Formation of CuNPs on the surface of Meso-ZSM-5 was also investigated using DRUV-visible spectroscopy (Fig. S2, ESI). In general, absorptions in the range of 250-450 nm are ascribed to charge transfer bands, whereas absorptions above 620 nm are ascribed to d-d transition.[16] In addition, absorption above 500 nm belongs to plasmonic resonance of Cu_n nanoparticles.[16] In this study, no absorption in the range of 400-1000 nm is observed in Meso-ZSM-5. However, it is clearly observed in Cu(10%)/Meso-ZSM-5. The visible range absorption can be assigned to the plasmonic resonance produced by Cu_n nanoparticles.

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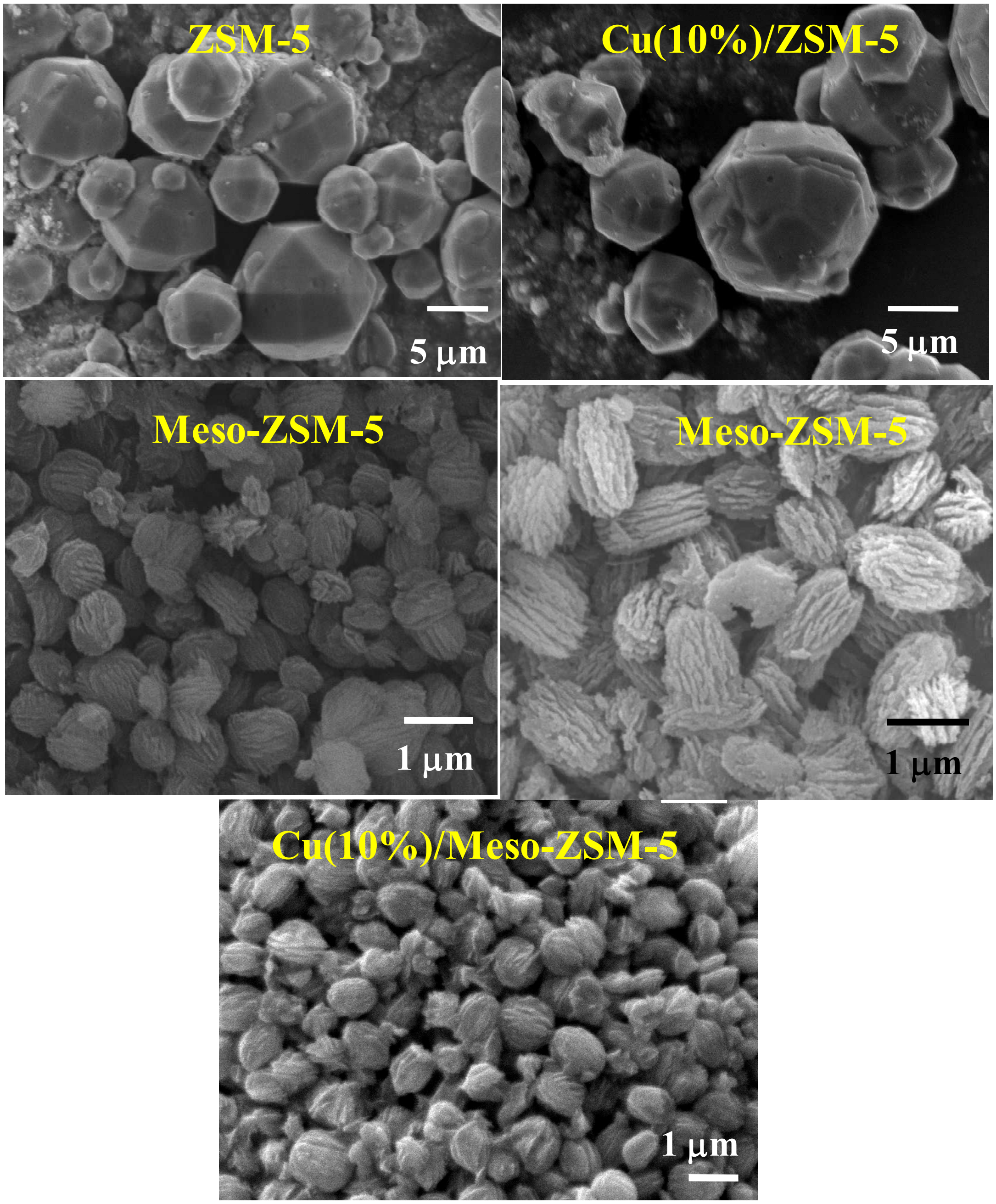

Fig. 2. SEM micrographs of parent and CuNPs decorated ZSM-5 and Meso-ZSM-5 samples.

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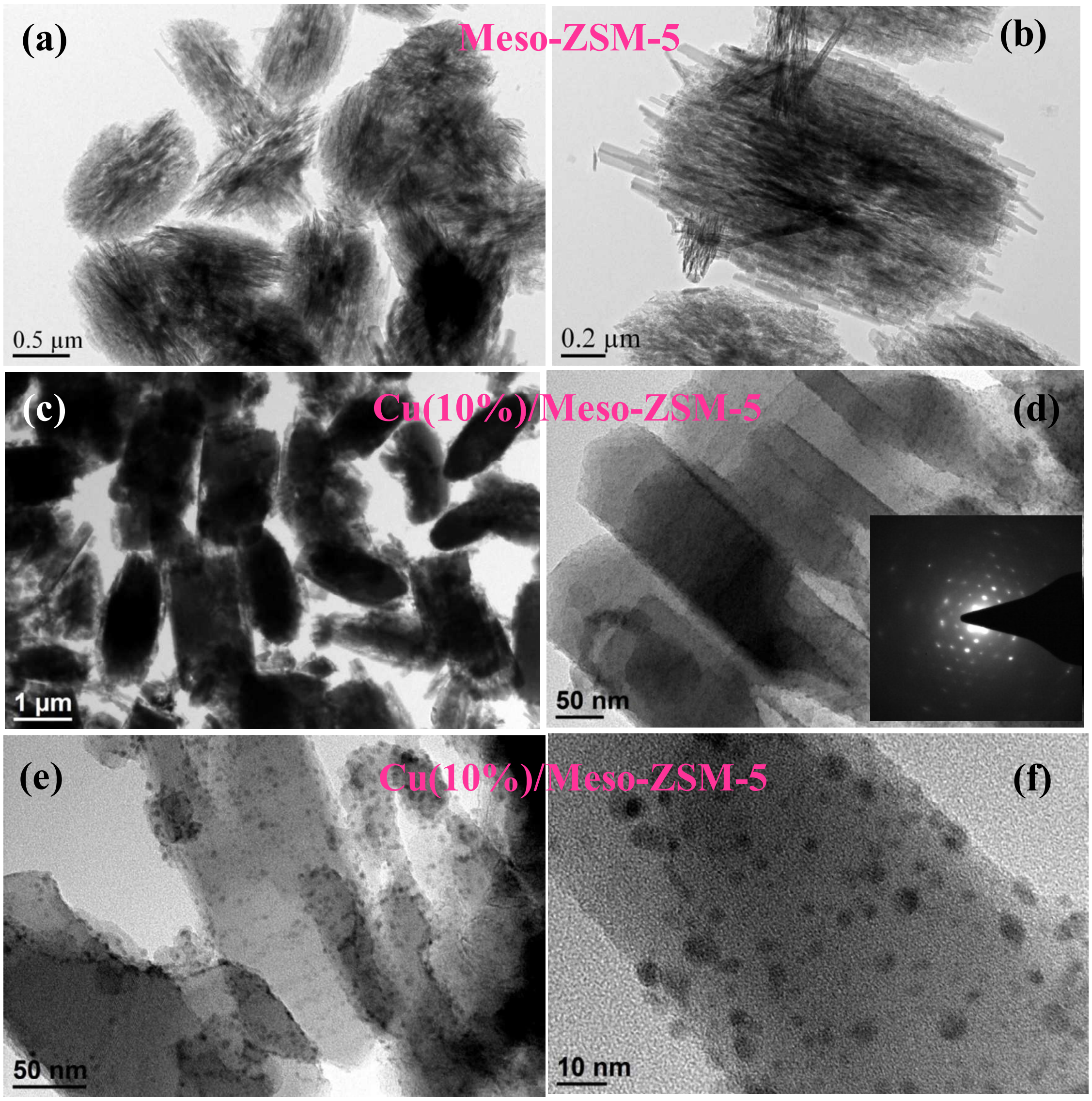

Fig. 3. TEM images of (a,b) Meso-ZSM-5 and (c-f) Cu(10%)/Meso-ZSM-5. Inset (d) shows the diffraction patterns obtained from the domain represented in (d).

3.2. Catalytic investigation

In this manuscript, efforts have been made to demonstrate the application of Cu^{2+} ion-exchanged and Cu nanoparticles decorated mesoporous zeolites in the synthesis of large organic molecules such as indolizines, chalcones, and 1,2,3-triazoles by using phenylacetylene as one of the building blocks.

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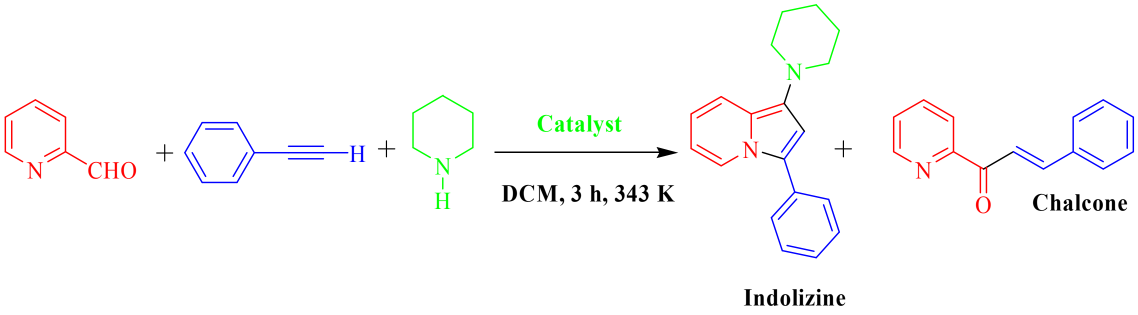
Table 2. Catalytic activity data obtained in the synthesis of indolizine in dichloromethane over various catalysts investigated in this study.



E.No	Catalyst	2-Pyridinecarboxaldehyde conv.(%)	Product selectivity (%)	
			Indolizine	Chalcone
1	CuO	65.2	60.4	39.6
2	Cu-Meso-ZSM-5	55.3	100	0
3	Cu-HY	98.1	18.2	81.8
4	Cu-NaY	84.2	69.7	30.3
5	Cu(10%)/Meso-ZSM-5	77.5	100	0
6	Cu(5%)/Meso-ZSM-5	60.6	100	0
7	Cu(10%)/ZSM-5	38.2	100	0
8	Cu(10%)/SBA-15	60.5	100	0
9	Cu(10%)/Al_2O_3	46.1	70.6	29.4
10	Cu(10%)/Meso-ZSM-5 [a]	76.3	100	0
11	Cu(10%)/Meso-ZSM-5 [b]	91.8	100	0
12	Cu(10%)/Meso-ZSM-5 [c]	93.6	100	0

Reaction condition: 2-Pyridinecarboxaldehyde (1.0 mmol), piperidine (1.0 mmol), phenylacetylene (1.0 mmol), catalyst (40 mg), time (3 h), dichloromethane (DCM, 4 mL), reaction temp (343 K).

[a] Catalytic data obtained after the fifth recycles.

[b] Catalytic data obtained after the 4 h.

[c] Catalytic data obtained using 60 mg of catalyst.

Indolizine can be prepared by the conventional transition metal catalyzed C-N bond forming reaction.[17] In the recent time, efforts have been made to synthesize indolizines using Cu based homogeneous and heterogeneous catalysts.[18] In this study, effort is made to prepare indolizines by one-pot multi-component C-C coupling synthesis strategy which allows structural diversity in the sustainable atom-efficient, one-step synthesis route. We started our

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investigation to find which form of Cu containing species would be more suitable for the synthesis of indolizine. Experiments show that CuO is active for the synthesis of indolizine but the reaction is not very selective towards the formation of indolizine (Table 2). Chalcone is formed as side product. When the similar reaction is performed with Cu-Meso-ZSM-5 or Cu(10%)/Meso-ZSM-5 then indolizine is obtained as selective product (Table 2). The reactivity of Cu(10%)/Meso-ZSM-5 is found to be more when compared to Cu-Meso-ZSM-5 under the identical reaction condition. If one compares the Cu content in both these samples, then also the reactivity of Cu(10%)/Meso-ZSM-5 is more when compared to Cu-Meso-ZSM-5 (Table 1 and Table 2). It may be noted that amount of Cu ion-exchange depends on the amount of exchangeable cations present in the zeolite sample. To investigate the role of Cu^{2+} concentration in the zeolite sample, Cu-HY and Cu-NaY were also investigated. It is found that using these catalysts, in addition to indolizine, chalcone is also formed as side product. It is interesting to note that reaction is found to be more selective for chalcone when HY is used when compared to NaY. This provides evidence that acid sites present in the catalyst would be favorable for the synthesis of chalcone. The role of CuNPs is to activate the phenyl acetylene terminal acidic proton and form Cu-acetylide, which is one of the key steps in the multi-component synthesis of indolizine. As shown in Table 1 that the synthesis of indolizine is favoured if the support is basic or even neutral. Since CuO is somewhat acidic in nature, therefore it would result in the formation of substantial amount of chalcone as we obtained in the case of acidic CuNPs/HY. Since amount of Cu nanoparticles can be finely tailored and indolizine can be selectively prepared, therefore Cu nanoparticles supported Meso-ZSM-5 would be better for the selective synthesis of indolizine. Under the optimized reaction condition, Cu(10%)/ZSM-5 exhibits less product yield (Table 2). Catalytic investigations show that the yield of indolizine can be easily improved by increasing the reaction time or amount of the catalyst (Table 2). This provides evidence that large external surface area is beneficial for the synthesis of highly dispersed Cu nanoparticles that facilitates this reaction. Using Cu(10%)/Meso-ZSM-5, more number of active sites are accessible to the reactants that facilitate the multi-component reaction. To further evaluate the superiority of this catalytic system, Cu-Meso-ZSM-5 and Cu(10%)/Meso-ZSM-5 were recycled for the synthesis of indolizine. Progressive decrease in the activity is observed in Cu-Meso-ZSM-5 whereas no significant change in the activity is observed in the case of Cu(10%)/Meso-ZSM-5 (Fig. S3, ESI). This provides evidence that Cu^{2+} leach to solution and catalyzes the reaction. Leaching experiments further confirm that conversion increases even after the removal of the catalyst. Based on the recycling and leaching experiments one can conclude that Cu(10%)/ Meso-

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ZSM-5 is found to be sustainable and robust catalyst for the synthesis of indolizine (Table 2). Physico-chemical characterization shows that the textural properties and Cu content of the recovered catalyst are almost similar to that of fresh catalyst (Table 1).

Based on the results obtained in this work, one can conclude that highly dispersed CuNPs supported on Na form of ZSM-5 nanosheet is best suited for this reaction. Cu-Meso-ZSM-5 exhibits higher selectivity when compared with Cu-NaY, which clearly shows that reaction is favourable when support is basic and contains less Al in its framework. Since NaY has very large Al content (Si/Al = 2.5) in its framework, therefore, it will impart some acidity even in the Na form, therefore it exhibits low selectivity for indolizine. This can also be correlated from the results obtained using Cu(10%)/SBA-15 and Cu(10%)/Al_2O_3. SBA-15 has large surface area (even somewhat higher than Meso-ZSM-5) but it possess small acidity that is not favourable to obtain high yield of indolizine. However, it may be noted that in the case of SBA-15, only indolizine is obtained as selective product. It may be noted that SBA-15 is prepared in acidic medium and it will exhibit very low acidity even in the absence of Al in the amorphous mesoporous framework structure. Less surface area and bi-functional nature (acidic and basic sites) of the Al_2O_3 are responsible for the low conversion and selectivity for indolizine. Based on the results obtained one can clearly say that favourable metal support interaction between CuNPs and Na form of Meso-ZSM-5 nanosheet leads to provide interesting catalytic properties. In order to validate this conclusion, CuNPs supported Na-form of Nano-Beta[5a] (Si/Al = 19) (Surface area = 672 m^2/g) and CuNPs supported Meso-ZSM-5 (with Si/Al = 50) (Surface area = 608 m^2/g) were prepared and investigated. The activity of Cu(10%)/Nano-Beta (Conversion = 77.9 %, Selectivity = 100 %) and Cu(10%)/Meso-ZSM-5 (Si/Al = 50) (Conversion = 76.7 %, Selectivity = 100 %) were found to be similar. These results clearly demonstrate that the optimum basicity of support, large surface area, favourable metal-support interactions, highly dispersed active metal centres, all are important to achieve high activity and selectivity.

Influence of solvent in the synthesis of indolizine is investigated and data is presented in Fig. 4. Reaction did not proceed in toluene. Very low yield of indolizine is obtained in the protic solvent such as methanol. However, only indolizine is obtained as selective product in methanol. Polar aprotic solvent such as dichloromethane (DCM) and acetonitrile are investigated. Catalytic data shows that DCM is more effective and produced indolizine as selective product in excellent yield. However, using acetonitrile, not only the 2-pyridine carboxaldehyde conversion is low but the indolizine selectivity is also low. In order to see the general applicability of this protocol for wide range of amine derivatives, primary, secondary

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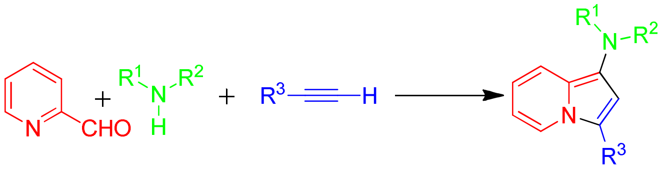
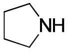
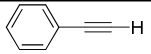
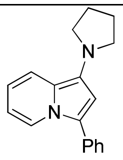
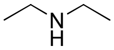
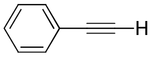
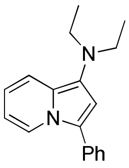
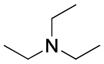
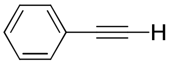
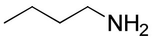
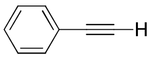
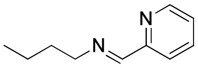
and tertiary amines were investigated (Table 3). Tertiary amine such as triethyl amine is found to be inactive under the optimized reaction condition (Table 3). When primary amine is reacted under the optimized reaction condition, indolizine is not obtained. In this case, condensation product of 2-Pyridine carboxaldehyde and n-butyl amine is obtained (Table 3). Reaction proceeds well with various secondary amines such as piperidine, pyrrolidine, and diethyl amine. In all these cases corresponding indolizine product is obtained (Table 3). However, reactivity varies by varying the amines. Diethyl amine is found to be the most reactive under the present reaction condition (Table 3). This difference in the reactivity can be attributed to the ring strain and steric factor. Wide range of phenylacetylene and secondary amines can be converted to corresponding indolizine with good to excellent yield (Table 3). It may be noted that the catalytic activity data presented in Table 3 are under the optimized reaction condition. Product yield can be easily improved by increasing the amount of catalyst or reaction time.

Table 3. Synthesis of indolizines using Cu(10%)/Meso-ZSM-5



Base	Phenylacetylene derivatives	2-Pyridine carboxaldehyde conv. (%)	Product selectivity (%)
		76.1	 (100%)
		96.0	 (100%)
		0	–
		99.8	 (100%)

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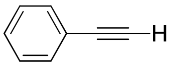
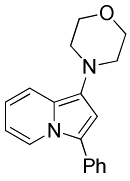
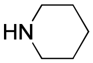
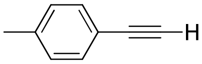
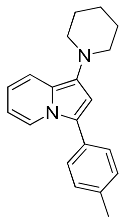
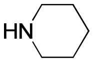
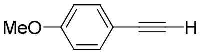
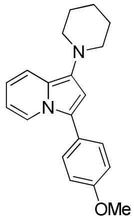
		67.2	 (100%)
		63.5	 (100%)
		77.9	 (100%)

Reaction condition: As mentioned in Table 2.

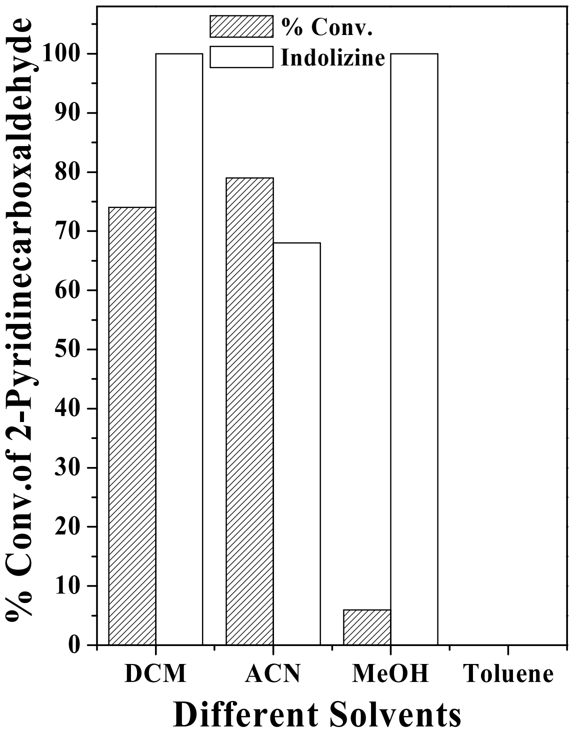


Fig. 4. Influence of solvent in the synthesis of indolizine using Cu(10%)/Meso-ZSM-5.

Based on the results obtained, following reaction mechanism is presented for the synthesis of indolizine (Scheme 1). In this multi-component synthesis methodology iminium

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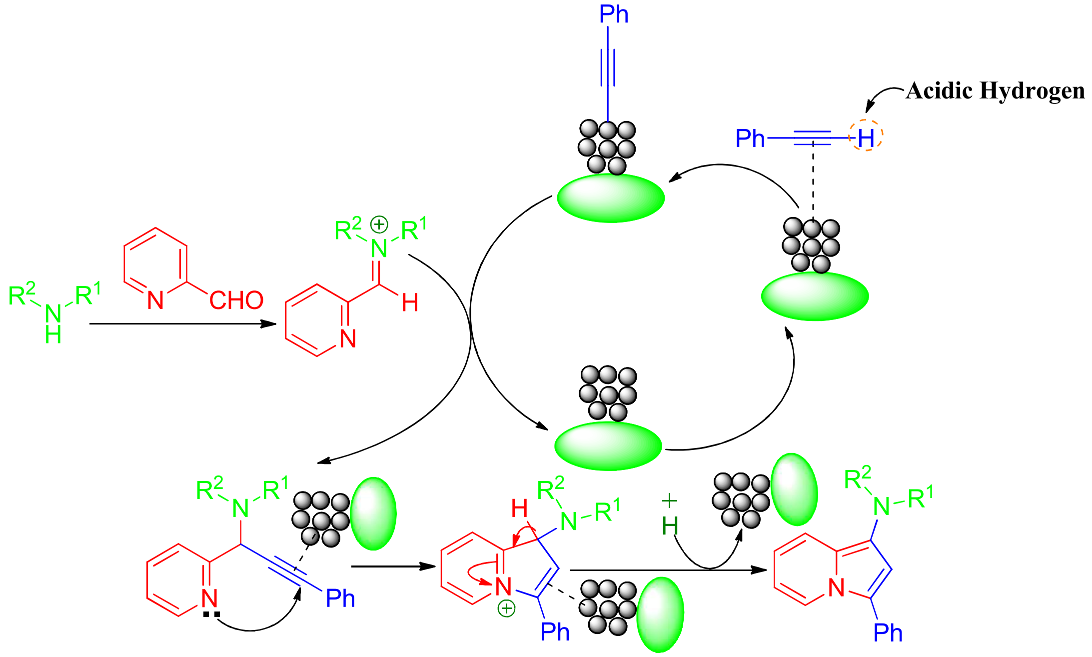
ions and Cu-acetylide would form first. Iminium ion would form by the condensation of amine (piperidine) and aldehyde (pyridine 2-carboxaldeyde). Furthermore, metal nanoparticles are known to activate the phenylacetylene acidic proton by the coordination to C-C triple bond to form Cu-acetylide. These two reactive components would cycloisomerize and aromatize in the presence of Cu catalyst to produce indolizine as the selective product. The presented mechanism is in accordance with the previous literature report.[18a]



Scheme 1. Plausible mechanism for the synthesis of indolizine by the multi-component reaction of 2-pyridine carboxaldehyde, amine and phenylacetylene.

Having shown the selective synthesis of indolizine, we were interested to find the suitable reaction condition for the selective synthesis of chalcone from 2-Pyridine carboxaldehyde and phenylacetylene under our experimental set-up. During the selective synthesis of indolizine, we found that solvent and catalyst both were important for the selective synthesis of indolizine. Similar results were obtained in one of the recent manuscript.[18a] Reaction investigations reveal that chalcone can be selectively obtained when the reaction is performed in neat condition using Cu(10%)/Meso-ZSM-5 (Table 4). Various other catalysts are also investigated under neat condition in this study (Table 4). Using CuO, in addition to chalcone, 2, 2’-bipiperidine is also formed. It is interesting to note that in this case, Cu-Meso-ZSM-5 or Cu-NaY is found to be inactive whereas Cu-HY is found to be

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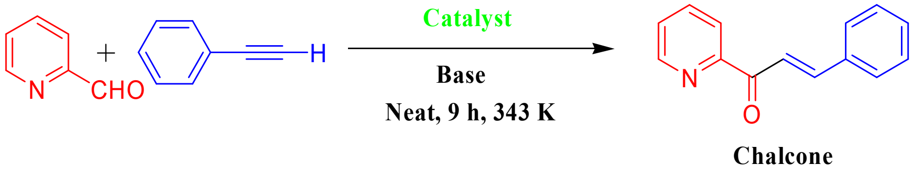
active (Table 4). However, Cu-HY produced both, chalcone and indolizine, under the optimized reaction condition. These results confirm that Cu^{2+} is not suitable for this reaction, whereas Cu nanoparticle is found to be active and selective for the synthesis of chalcone. In this case also, the activity of Cu(10%)/ZSM-5 is found to be low when compared to Cu(10%)/Meso-ZSM-5 (Table 4).

Table 4. Selective synthesis of chalcone in neat condition using Cu catalysts investigated in this study.



E.No	Catalyst	2-Pyridine carboxaldehyde conv. (%)	Product selectivity (%)		
			Chalcone	Indolizine	Other
1	CuO	98.2	74.2		25.8
2	Cu-Meso-ZSM-5	0	-	-	-
3	Cu-HY	53.1	55.4	44.6	-
4	Cu-NaY	0	-	-	-
5	Cu(10%)/Meso-ZSM-5	100	100	-	-
6	Cu(5%)/Meso-ZSM-5	76.4	100	-	-
7	Cu(10%)/ZSM-5	54.3	100	-	-
8	Cu(10%)/SBA-15	64.8	100	-	-
9	Cu(10%)/Al_2O_3	46.7	77.5	22.5	
10	Cu(10%)/Meso-ZSM-5[a]	100	100	-	-

Reaction condition: 2-Pyridine carboxaldehyde (1.0 mmol), piperidine (1.0 mmol), phenylacetylene (1.0 mmol), catalyst (40 mg), reaction time (9 h), reaction temp (343 K).
[a]Catalytic data obtained after the fifth recycles.

Influence of bases used in the synthesis of chalcone is also investigated (Table 5). Triethylamine is found to be inactive for this reaction, whereas primary amine such as butyl amine produced chalcone in low yield (Table 5). In addition to chalcone, condensation

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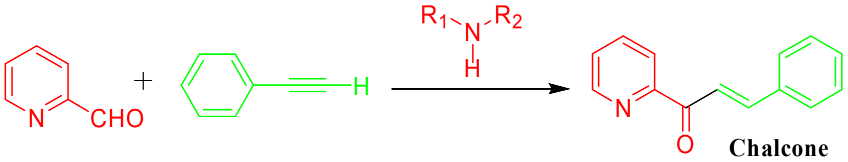
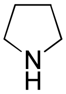
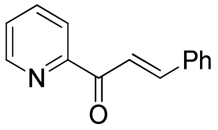
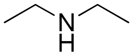
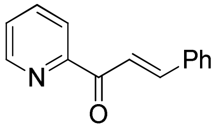
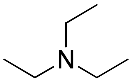
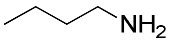
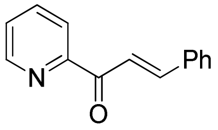
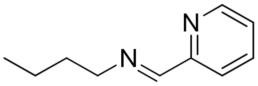
product of butyl amine and pyridine 2-carboxaldehyde is also obtained in large amount. Secondary amine is found to be excellent in assisting this reaction to form chalcone as selective product (Table 5). Almost quantitative yield of chalcone is obtained using various secondary amines such as piperidine, pyrrolidine, and diethylamine (Table 5). Cu(10%)/ Meso-ZSM-5 is recycled in the synthesis of chalcone. Recycling study shows that no significant change in the activity and selectivity is obtained even after five recycles, justifying robustness of the catalyst system (Table 4). In this case also optimum metal-support interaction between CuNPs and Na form of Meso-ZSM-5 nanosheet is responsible for the high catalytic activity as explained above in the case of indolizine.

Table 5. Role of amines in the selective synthesis of chalcone using Cu(10%)/Meso-ZSM-5.



Base	2-Pyridine carboxaldehyde conv. (%)	Products Selectivity (%)
	98.9	 (100%)
	99.7	 (100%)
	0	–
	99.8	 (74.7 %)  (25.3 %)

Reaction condition: 2-Pyridinecarboxaldehyde (1.0 mmol), base (1.0 mmol), phenylacetylene (1.0 mmol), catalyst (40 mg), reaction time 9 h, reaction temp (343 K).

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Results obtained using primary amine provides evidence that iminium ions produced by the condensation of pyridine 2-carboxaldeyde and secondary amine certainly participate in the reaction process. Considering this aspect, following mechanism is presented (Scheme 2). In this case, secondary amine has two roles to play: first, it acts as a reactant for the formation of iminium ion and second, it acts as a good base in this reaction. First few steps are the same as outlined in the mechanism for the synthesis of indolizine. In this case, reaction takes place in the absence of solvent, therefore the basicity of secondary amine would predominate and reacts with the intermediate formed by the reaction between iminium ion and Cu-acetylide to form allenyl amine. The negative inductive effect produced by the electron withdrawing group increases the acidity of proton attached to propargyl hydrogen atom and stabilizes the negative charge produced after the deprotonation of propargyl-allenyl amine intermediate. Hydrolysis of the propargyl-allenyl amine intermediate takes place (by the H_2O formed in the initial condensation step) to form chalcone. The presented mechanism is in accordance with the previous literature report.[18a] Catalytic activity of Cu(10%)/Meso-ZSM-5 in the synthesis of indolizine/chalcone using phenylacetylene is either similar or higher when compared to reported literature.[18]

As outline in the mechanism of chalcone synthesis that basicity of amine is very important. Only secondary amine is able to produce chalcone. Basicity of amine plays decisive role in the synthesis of chalcone. Based on the results one can say that the unsolvated diethylamine is acting as more efficient base when compared to solvated diethyl amine. Since the acidity and basicity is highly depended on the reaction medium, one can say that the basicity of secondary amine is found to be the optimum in the synthesis of chalcone under neat condition. Based on the result, one can say that DCM favors the formation of indolizine through cycloisomerization of pyridinyl propargylamine as intermediate. In DCM, rearrangement of the pyridinyl propargylamine intermediate takes place to form the product. Whereas under neat condition, pyridinyl propargylamine does not undergo rearrangement and reaction follows different pathway due to the high basic strength of secondary amine in neat condition. In this case the abstraction of proton associated to pyridinyl propargylamine takes place that leads to form allenyl amine intermediate, which upon hydrolysis leads to form chalcone.

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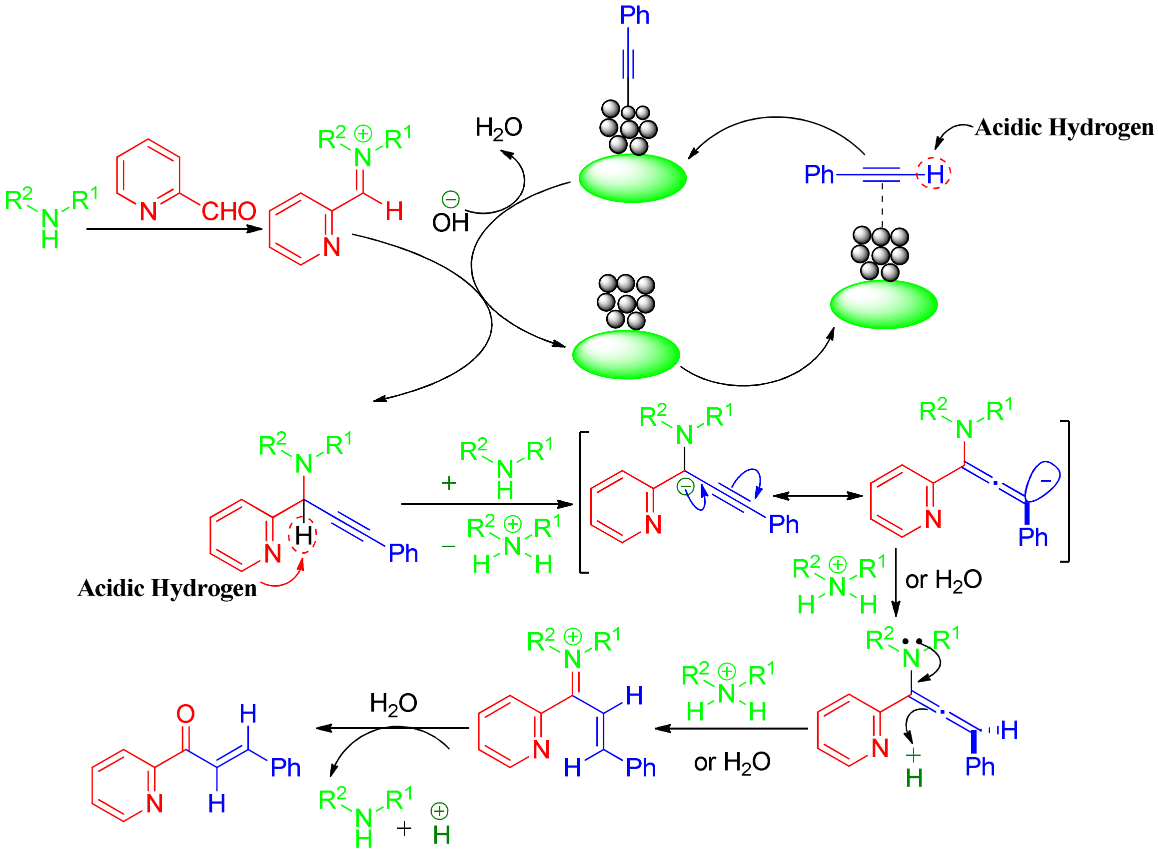

Scheme 2. Plausible mechanism for the synthesis of chalcone by the multi-component reaction of 2-pyridine carboxaldehyde, amine, and phenylacetylene.

These reactions involve large organic molecules that cannot be able to diffuse into the micropores of the materials. It may be noted that reaction proceeds even with CuO or Cu/Al_2O_3. These results clearly show that zeolite microporosity has no role to play in these reactions. In these reactions, oxidation state of Cu and dispersion of CuNPs at the large external surface of Meso-ZSM-5 are more important when compared to the micropores and inter/intra crystalline mesopores of Meso-ZSM-5. Since CuNPs (Cu(0)) could activate the phenyl acetylene terminal acidic proton easily when compared to CuO (Cu(II)), therefore CuNPs supported catalysts exhibited higher activity. Cu(10%)/Meso-ZSM-5 exhibited higher product yield when compared to Cu(10%)/ZSM-5. This clearly shows that the highly dispersed active CuNPs are present at the large external surface of Meso-ZSM-5, which enhances the accessibility of large number of the reactant molecules when compared to Cu(10%)/ZSM-5 that are responsible for the high activity of Cu(10%)/Meso-ZSM-5.

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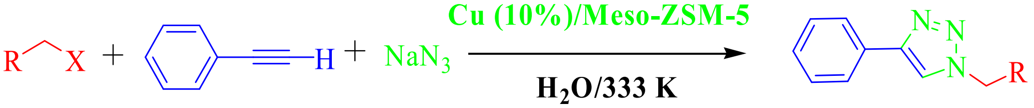
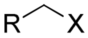
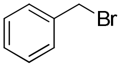
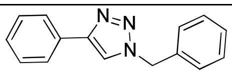
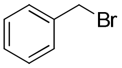
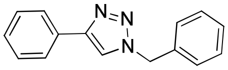
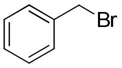
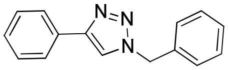
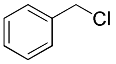
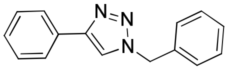
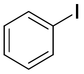
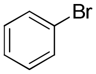
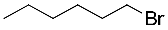
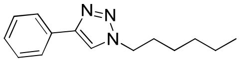
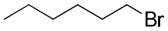
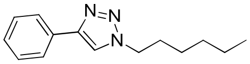
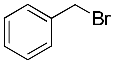
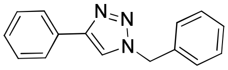
Table 6. Synthesis of 1,4-disubstituted, 1,2,3-triazole using benzyl/aliphatic halides as reactant using Cu nanoparticles supported ZSM-5 catalysts.



E.No.		Catalyst	Product (%Yield)
1		Cu(10%)/Meso-ZSM-5	 (96.4)
2		Cu(5%)/Meso-ZSM-5	 (62.1)
3		Cu(10%)/ZSM-5	 (50.4)
4		Cu(10%)/Meso-ZSM-5	 (80.3)
5		Cu(10%)/Meso-ZSM-5	Nil
6		Cu(10%)/Meso-ZSM-5	Nil
7		Cu(10%)/Meso-ZSM-5	 (55.2)
8[a]		Cu(10%)/Meso-ZSM-5	 (94.3)
9[b]		Cu(10%)/Meso-ZSM-5	 (93.2)

Reaction condition: Benzyl chloride (2 mmol), sodium azide (2 mmol), phenylacetylene (2 mmol), H_2O (4 mL), catalyst amount (40 mg), reaction temperature (343 K), reaction time (6 h). [a]Catalytic data obtained after the 14 h. [b]Catalytic data obtained after the fifth recycles.

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Having shown the application of this robust catalyst system in the synthesis of indolizine and chalcone, it is important to show the application of the catalyst in other multi-component reactions where phenylacetylene can be used as building block. We were interested to explore the possibility to use phenylacetylene as building block for the construction of other functionalized organic substructures, which are precursors for the synthesis of many industrial products, molecular materials and bioactive compounds. Multi-component reaction strategy can be used to synthesize 1,2,3-triazole derivatives using phenylacetylene as one of the reactant.[19] In general, for the synthesis of 1,2,3-triazole, aromatic azides are chosen as one of the reactant.[19] However, aromatic azides are costly. Therefore attempts are made in this study to use sodium azide as economical azide precursor for the synthesis of 1-benzyl-4-phenyl-1H-1,2,3-traizole.[20] In recent time, efforts have been made to synthesize triazole derivatives using Cu based homogeneous and heterogeneous catalysts.[20] Herein, we have explored the possibility to use in-situ generated aromatic azides (from suitable precursors) in one pot synthesis of 1,2,3-triazoles. In this manuscript benzyl halide and epoxides are chosen to obtain functional 1,4-disubstituted 1,2,3-triazoles. First reaction condition was optimized using benzyl bromide, phenylacetylene, and sodium azide in H_2O as green reaction medium with Cu(10%)/Meso-ZSM-5 catalyst. Reaction proceeds well using this catalyst and produced 1,4-disubstituted, 1,2,3-triazole compound as selective product (Table 6). Product was confirmed with NMR spectroscopy that matches well with the reported literature. The reaction also proceeds with Cu(10%)/ZSM-5 but low yield of the product is obtained. This provides further evidence that the Meso-ZSM-5 support is ideal for the synthesis of large molecules such as substituted 1,2,3-triazoles. The reaction proceeds faster when benzyl bromide is used as reactant when compared to benzyl chloride (Table 6). Reaction also takes place when aliphatic bromide such as bromohexane is reacted (Table 6). However, it requires longer reaction time to afford good yield. It may be noted that reaction did not proceed with iodobenzene or bromobenzene. The reusability of Cu(10%)/Meso-ZSM-5 was examined by the model reaction of phenylacetylene, benzyl bromide, and sodium azide and the results are given in Table 6. It is observed that after five recycles, the product yield is only marginally lower when compared to the fresh catalyst, which indicates that Cu(10%)/Meso-ZSM-5 exhibits high catalytic activity and stability under our experimental condition. To present the mechanism of this reaction, two control experiments were performed. In the first control experiment, first benzyl bromide is reacted with sodium azide followed by the reaction with phenylacetylene to afford the desired product (Scheme 3). The yield (91 %) of this two step reaction is somewhat lower when compared to one-pot multi-

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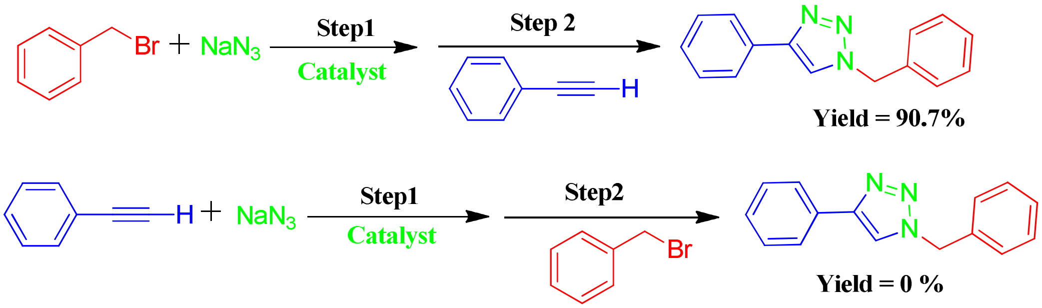
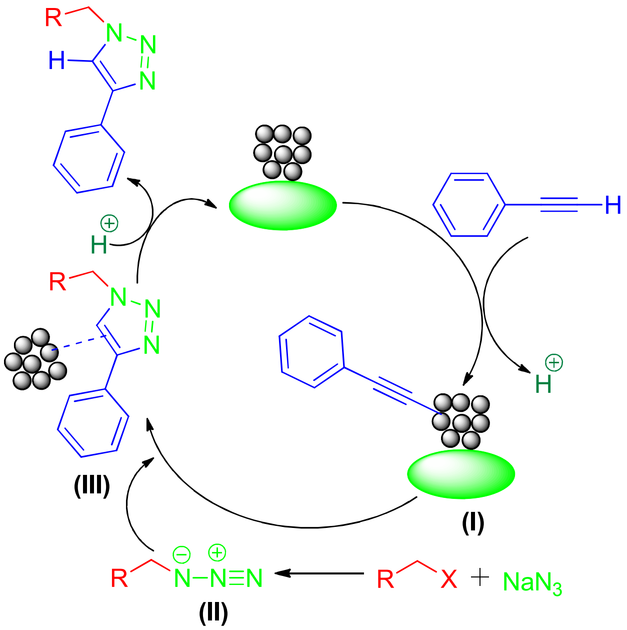
component reaction of the present investigation. In second control reaction, first phenylacetylene is reacted with sodium azide followed by the reaction with benzyl bromide. In this two-step process, desired product 1-benzyl-4-phenyl-1H-1,2,3-traizole is not obtained. Based on these observations, reaction mechanism is presented (Scheme 4). As mentioned above in the synthesis of indolizine, in this case also, Cu nanoparticles would react with phenylacetylene and form Cu-acetylide (Intermediate I). Meanwhile, benzyl bromide would react with sodium azide to form benzyl azide (Intermediate II). In-situ formed benzyl azide would react with Cu-acetylide to form Intermediate III, which abstracts H^+ (that was generated in the first step of the reaction) and lead to form desired product and the catalyst is regenerated.



Scheme 3. Exploration of reaction pathways involved in the synthesis of 1,4-disubstituted 1,2,3-triazoles.



Scheme 4. Plausible mechanism for the synthesis of 1,4-disubstituted 1,2,3-triazoles by the multi-component reaction of phenylacetylene, benzyl/aliphatic halides and sodium azide.

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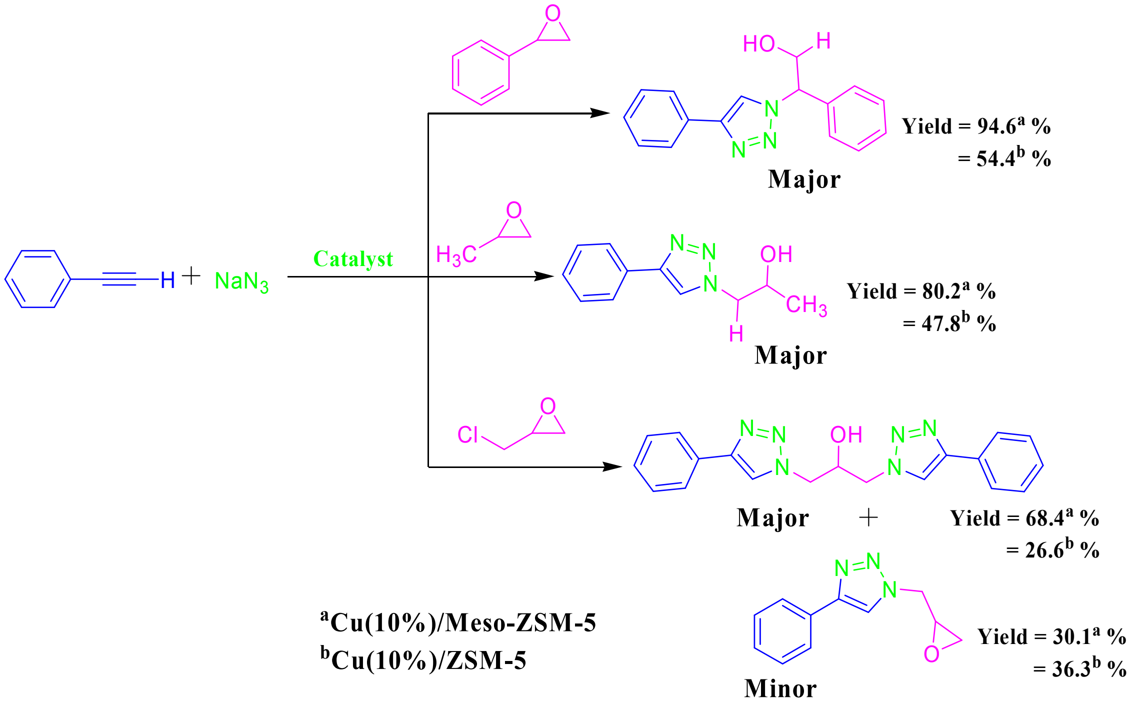

Scheme 5. Influence of epoxides in the product selectivity during the multi-component reaction of phenylacetylene, sodium azide and epoxide over CuNPs decorated ZSM-5 nanosheets. Reaction condition: Epoxides (2.0 mmol), sodium azide (2.0 mmol), phenylacetylene (2.0 mmol), water (4 mL), catalyst (40 mg), reaction time (6 h), reaction temp (343 K).

Having successful in the synthesis of 1,4-disubstituted 1,2,3-triazole using halide reactant, aromatic and aliphatic epoxides were reacted under the same condition to obtain β-hydroxy, 1,4-disubstituted 1,2,3-triazoles (Scheme 5). This reaction depends on the nature of epoxide and can be grouped in three categories: aromatic epoxide such as styrene oxide and its derivative, aliphatic epoxide such as propylene oxide or other aliphatic linear chain based epoxides and halogen based epoxide such as epichlorohydrin. In all three cases, three different types of products are obtained (Scheme 5). When styrene oxide is reacted it forms primary alcohol based β-hydroxy, 1,4-disubstituted 1,2,3-triazoles [2-Phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol] (isolated yield = 94.6%) selectively, whereas when propylene oxide is reacted, then secondary alcohol based β-hydroxy, 1,4-disubstituted 1,2,3-triazole [1-(4-Phenyl-1H-(4-phenyl-1,2,3-triazol-1-yl) propan-2-ol] (isolated yield = 80.2%) is selectively obtained. Thin layer chromatography investigation shows that, in these cases trace amount of other regioisomer is also formed during the reaction, which is somewhat difficult to isolate using column chromatography. Mechanism of this reaction can be explained based on the ring opening of epoxide with sodium azide. Azide ion opens the oxirane ring

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differently due to the formation of more stable species as illustrated in the proposed mechanism that leads to form two different regioisomers in these two cases. Cu nanoparticles activate the epoxide ring and N_3^- opens the oxirane ring to form azido alcohol intermediate (I) (Scheme 6).[21] In the mean time, a π-complex is simultaneously formed between phenylacetylene and Cu nanoparticles to afford the copper(II) acetylide intermediate (II). Then, 1,3-dipolar cycloaddition between these two intermediates (I) and (II) would take place to form copper(II) β-hydroxytriazolide intermediate (III), which rearranges to intermediate (IV). Protonolysis of intermediate (IV) takes place to afford corresponding β-hydroxy-1,2,3-triazole selectively in high yield. ^1H and ^{13}C NMR of the isolated products confirmed the formation of two different regioisomers obtained using styrene oxide and propylene oxide (Figs. S5-S8, ESI). When the same reaction is performed with epichlorohydrin, bis-triazole (1,3-bis(5-phenyl-1H-1,2,3-triazol-1-yl) propan-2-ol**]** is obtained as selective product (isolated yield = 68.4%), which was confirmed with ^1H, ^{13}C, and ^1H-^{13}C HETCOR NMR investigations (Figs. S9-S12, ESI). This product is formed because, Cl^- is a good leaving group that reacts with sodium azide to form azide derivative of epoxide similar to the proposed reaction for benzyl bromide/chloride with sodium azide (Intermediate I, Scheme 7). Azide derivative of epoxide reacts with phenylacetylene to form Intermediate II (Scheme 7). This intermediate is isolated as minor product (isolated yield = 30.1%) during the reaction (Scheme 5) (Fig. S12, ESI). Ring opening of Intermediate II would take place to form Intermediate III (Scheme 7), which would react with phenylacetylene to form bis-triazole as major product (Scheme 7). The activity of Cu(10%)/ZSM-5 is significantly low when compared to Cu(10%)/Meso-ZSM-5 in this reaction, which confirms that Meso-ZSM-5 is more suitable for this reaction (Scheme 5). Cu(10%)/Meso-ZSM-5 was easily recycled five times with no appreciable loss in the activity during the multi-component reactions of phenylacetylene, styrene oxide and sodium azide. Upon completion of the reaction, the catalyst was recovered from the reaction mixture by simple filtration, washed with ethyl acetate followed by distilled water, dried at 373 K in an oven for 6 h, and was then used in the next cycle. The recovered catalyst exhibits remarkable consistent catalytic activity during five cycles (Fig. S13, ESI). Catalytic activity of Cu(10%)/Meso-ZSM-5 in the synthesis of 1,4-disubstituted 1,2,3-triazoles using phenylacetylene is either similar or higher when compared to reported literature.[20]

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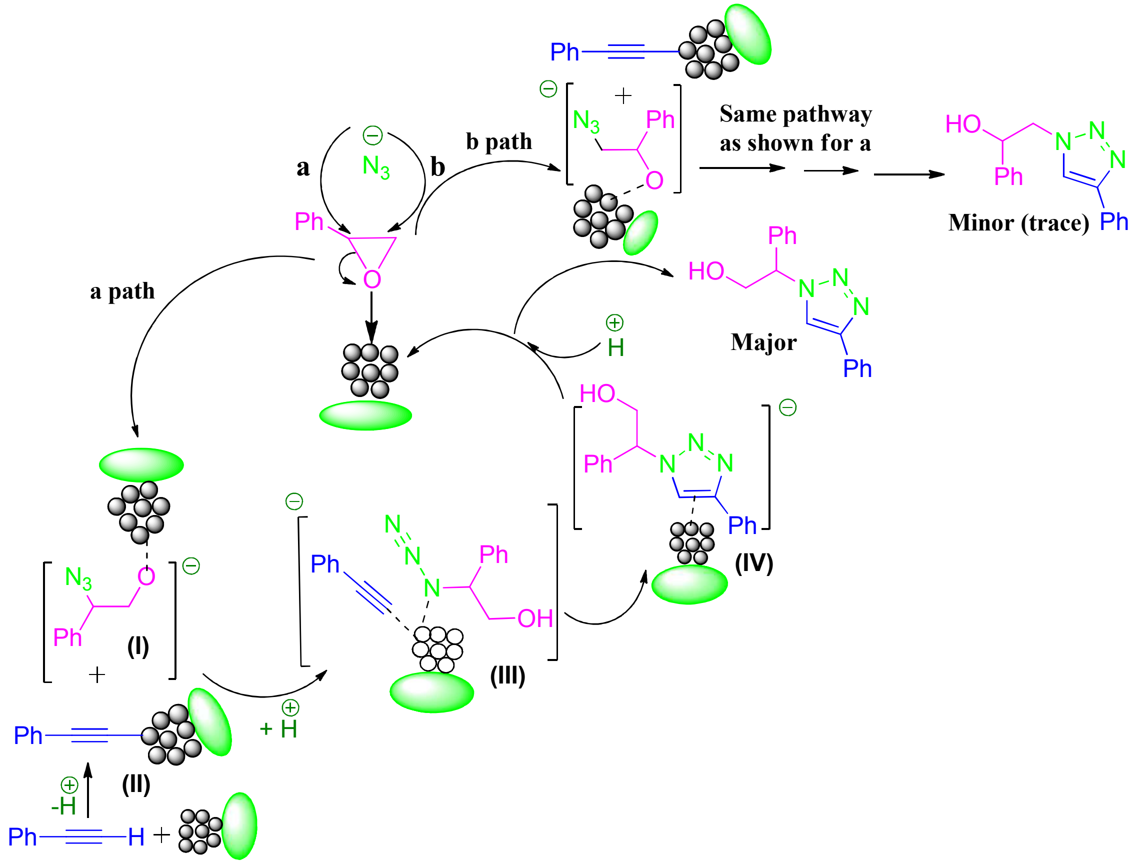
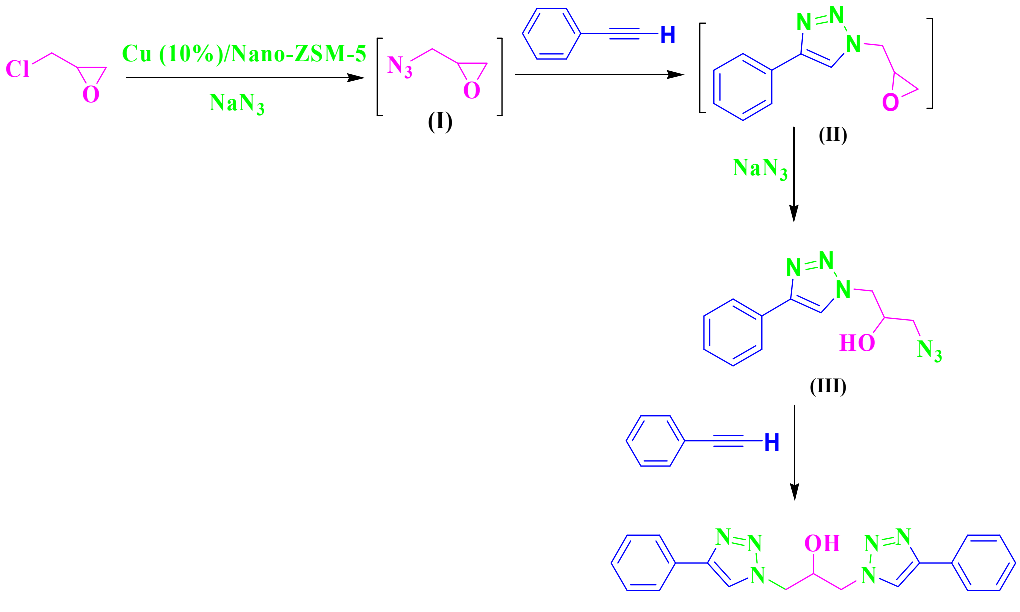


Scheme 6. Plausible mechanism involved during the multi-component reaction of phenylacetylene, sodium azide and aromatic/aliphatic epoxide over CuNPs decorated ZSM-5 catalysts.



Scheme 7. Proposed reaction steps involved in the synthesis of bis-triazole by the multi-component reaction of epichlorohydrin, phenylacetylene, and sodium azide.

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4. Conclusion

Cu nanoparticles decorated ZSM-5 nanosheet was successfully prepared. Physicochemical characterization reveals that highly dispersed 2-3 nm Cu nanoparticles were supported on the large external surface of Meso-ZSM-5. Cu nanoparticles supported Meso-ZSM-5 nanosheet exhibited excellent activity in the synthesis of large organic molecules when compared to Cu nanoparticles decorated microporous ZSM-5 zeolite. Catalyst exhibited excellent activity in the sustainable synthesis of indolizines, chalcones, and substituted triazoles by one-pot multi-component synthesis. Medium of reaction plays crucial role in the selective synthesis of indolizine/chalcone. When DCM was used as solvent, indolizine was selectivity obtained whereas in neat condition chalcone was selectively obtained. Cu nanoparticles decorated Meso-ZSM-5 exhibited better activity when compared to Cu^{2+} ion-exchanged Meso-ZSM-5. Catalyst can be easily recycled and exhibited no loss in the activity even after five recycles. Regiospecific 1,4-disubstituted 1,2,3-triazole can be prepared using Cu nanoparticles decorated Meso-ZSM-5. Regiospecificity was found to be dependent on the nature of epoxide. Aromatic and aliphatic epoxides offered different regioselectivity. Furthermore, epichlorohydrin afforded bis-traizole as selective product under the optimized reaction condition. High reactivity of Cu nanoparticles decorated Meso-ZSM-5 can be attributed to the optimum metal-support interaction, highly dispersed Cu nanoparticles that could be easily accessible to large reactant molecules, and the facile diffusion of product molecules from the active centres through inter/intra-crystalline mesopores of Meso-ZSM-5. Large external surface and mesopores enable the active sites to be available for further reaction, which makes this catalyst recyclable and sustainable. Further work in this direction is underway to develop economical metal nanoparticles based sustainable catalytic process for selective synthesis of unique molecules of therapeutic importance.

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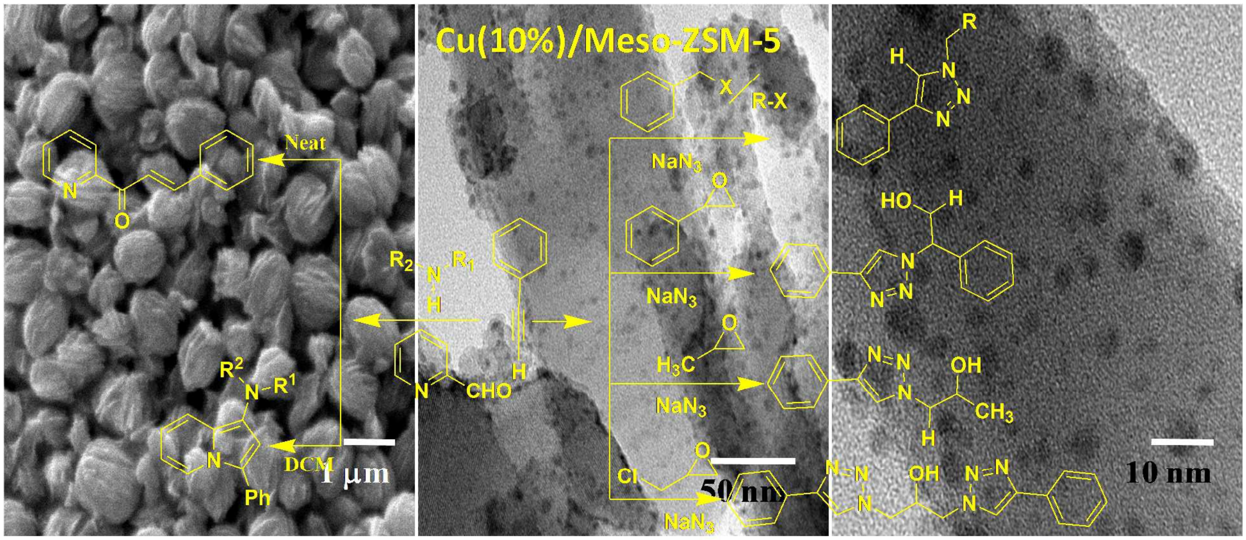
Table of Contents

Cu ion-exchanged and Cu nanoparticles decorated mesoporous ZSM-5 catalysts for the activation and utilization of phenylacetylene in the sustainable chemical synthesis

Bhaskar Sarmah, Biswarup Satpati, and Rajendra Srivastava*



Highly dispersed Cu nanoparticles supported on the large external surface of Meso-ZSM-5 exhibited excellent activity in the selective synthesis of indolizines, chalcones, and triazoles using phenylacetylene as one of the building blocks.