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Efficient Three-Components Coupling Reactions Catalyzed by Cu⁰-nanoparticles stabilized on Modified Montmorillonite

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Abstract

In situ generation of Cu⁰-nanoparticles into the nanopores of modified Montmorillonite and their catalytic performance in three components (A³) coupling reactions of aldehyde, amine and alkyne to synthesize propargylamines have been described here. The modification of Montmorillonite was carried out with HCl under controlled conditions for generating nanopores into the matrix and these pores act as “host” for *in situ* generation of Cu⁰-nanoparticles. The Cu⁰-nanoparticles were generated into the nanopores of acid activated clay mineral matrix by successful loading of Cu(CH₃COO)₂ metal precursor by incipient wetness impregnation technique followed by reduction with NaBH₄. TEM study reveals that Cu⁰-nanoparticles of size below 10 nm are evenly distributed on the support. The synthesized Cu⁰-nanoparticles exhibit face centered cubic (fcc) lattice. The Cu⁰-nanoparticles serve as efficient *green* and heterogeneous catalyst for three-component coupling *via* C-H alkyne-activation to synthesize propargylamines with excellent yields (82-94%) and 100% selectivity under mild reaction conditions without requiring any additives or inert atmosphere. The nanocatalysts can be recycled and reused several times without significant loss of their catalytic activity.

Keywords: Cu⁰-nanoparticles; Montmorillonite; Propargylamines; C-H activation; Heterogeneous catalyst

41 1. Introduction

42 Recently, in the route of development of *green* processes for the synthesis of fine
43 chemicals and bio-active molecules, the concept of atom economy / efficiency finds
44 considerable attention.¹ In this regards, an increasing number of multicomponent reactions
45 have been designed for the synthesis of diverse complex molecules through a combination of
46 three or more starting materials in one-pot, which reduces the waste and increasing safety as
47 well as reaction yield.² Among the different multicomponent reactions, the catalytic coupling
48 reaction of aldehyde, amine and alkyne (so-called A³ coupling) is one of the best examples,
49 where propargylamines are produced as the main product. Propargylamines are versatile
50 intermediates for the preparation of various nitrogen-containing compounds and are the key
51 components of biologically active pharmaceuticals and natural products.³ The
52 propargylamines derivatives have gain much importance after the pivotal discovery of
53 rasagiline (Azilect™), which is molecularly a propargylamine derivative used as a
54 monotherapy in early Parkinson's disease and some propargylamines derivatives also used as
55 potent anti-apoptotic agent and neuroprotective agent.⁴ Several classical methods are
56 available for the synthesis of propargylamines through addition of metallated alkynes to an
57 imine. The metallated alkynes are generated by using different strong bases such as
58 alkylmetals, metallated amides, alkoxides and hydroxides.⁵ However, these metal alkynylides
59 are relatively difficult to handle, because these are moisture sensitive and require strictly
60 controlled reaction conditions otherwise forms large amount of waste materials. In recent
61 years, various mid- and late transition metals catalyzed coupling of aldehydes, amines and
62 alkynes has become a powerful tool that facilitates the coupling of alkynes to imines
63 (generated *in situ*) via terminal alkyne C-H activation in a more efficient manner.^{3e-h,6} Among
64 the different metals, Cu(I), Cu(II) complexes and also various simple and inexpensive copper
65 halides salts are extensively utilized as catalysts for the A³-coupling reaction with secondary
66 amines.⁷ However, most of the catalytic systems are homogeneous in nature, but only few
67 reports on heterogeneous catalysts are available in the literature. Li and Wang reported an
68 efficient and reusable heterogeneous Cu(I) silica based organic-inorganic composite material
69 for the A³-coupling reaction under solvent free condition.⁸ Lei Wang and co-workers
70 prepared a silica supported complex of Cu(I) and an N-heterocyclic carbene and used it to
71 achieve high yield in the A³-coupling reaction.⁹ Besides silica based materials, other supports
72 like molecular sieves, zeolites etc. have also been used for immobilizing the Cu metal.^{6d,10}
73 But these catalytic systems often show several disadvantages. Most of the catalyst supports
74 are synthetic and required laborious and time-consuming effort for their synthesis as well as

75 surface functionalization, which may poison the catalytic active sites of the supports and the
76 particles, moreover, molecular sieves or zeolites like mesoporous matrixes in general exhibit
77 low or restricted pore sizes.

78 In the last decade, supported metal nanocatalytic systems are considered as
79 sustainable and competitive alternative to the conventional catalysis, due to high surface
80 reactivity and high surface-to-volume ratio of metal nanoparticles, which enhances their
81 activity and selectivity and more importantly they satisfied the stringent criteria of
82 heterogeneous catalyst.¹¹ Nowadays, nanoparticles of metals such as Cu, Au, Fe, In, etc. have
83 been used as substitutes of bulk metal in the various C-H activation reactions in order to
84 reduce the catalyst loading, reaction time and also to minimize the undesired
85 products.^{2a,3g,6a,11,12} Particularly, Cu⁰-nanoparticles supported on different supports have been
86 extensively utilized in the 1,3-dipolar cycloaddition of azides and terminal alkynes to
87 synthesize 1,2,3-triazoles.¹³ But, limited numbers of reports are available in the literature
88 which describes the use of supported Cu⁰- nanoparticles in A³ coupling reaction.^{12a,14}
89 Albaladejo et al. have reported an efficient catalytic system based on Cu⁰-nanoparticles
90 supported on TiO₂ for A³ coupling reaction and widely illustrated the substrate tolerance as
91 well as recyclability of the catalyst.^{12a} Although, homogeneous and heterogeneous catalysts
92 studied in A³ coupling reactions show good activity, there are still some drawbacks which
93 restrict their acceptance, such as high prices of the used precise metals and tedious catalyst
94 preparation methods. In addition, some catalytic systems used environmentally unacceptable
95 substances, harsh reaction conditions, long reaction times, and requirement for additives or
96 inert atmosphere. Therefore, the development of novel, efficient and recoverable catalytic
97 system for A³ coupling reactions is a great challenge for researchers. With these precedents in
98 mind and encouraged by our recent works,¹⁵ herein, we have reported a well-defined
99 heterogeneous catalytic system i.e. Cu⁰-nanoparticles supported on modified Montmorillonite
100 for A³ coupling reaction at mild reaction condition. These nanoparticles maintain their
101 catalytic efficiency for several cycles and serve as potential reusable catalyst. The modified
102 Montmorillonite is considered as environmentally benign, cheap, easily available and robust
103 support / stabilizer materials for the synthesis of different metal nanoparticles.¹⁵ Laszlo et al.
104 reported interesting Montmorillonite based catalytic system for organic synthesis.¹⁶ This
105 Montmorillonite is collected from the indigenous source i.e. natural deposits of western part
106 of India, which was purified and activated with mineral acid under controlled conditions to
107 generate a matrix having high surface area and contain micro- and mesopores with diameter
108 in the range 0-10 nm on the surface. These nano range pores act as “host” for *in situ*

109 generation of Cu⁰-nanoparticles and also limit the growth of the particles upto desired range.
110 The other added advantages of this catalyst support is that it requires no surface
111 functionalization and can be customized their pore sizes by applying controlled acid
112 activation.^{15a-d}

113 **2. Experimental Section**

114 **2.1. Preparation of Support**

115 Purified Na⁺-Montmorillonite (10 g) was taken into a 250 mL three necked round
116 bottom flask and 200 mL 4 M sulphuric acid was added to it. The resulting dispersion was
117 refluxed for 1 h. After cooling, the supernatant liquid was discarded and the activated
118 Montmorillonite was repeatedly washed with deionised water and finally dried in a hot air
119 oven at 50 ± 5 °C over night to obtain the solid product. The activated Montmorillonite was
120 designated as AT-Mont. The surface characterizations of activated Montmorillonite were
121 presented in Table 1.

122 **2.2. Preparation of Cu⁰-nanoparticles**

123 0.5 g of AT-Mont. was taken into a 100 mL beaker and 15 mL (0.254 mmol) aqueous
124 solution of Cu(CH₃COO)₂ was added slowly under vigorous stirring condition. The stirring
125 was continued for another 6 h followed by evaporation to dryness in a rotary evaporator. 0.3
126 g of dry clay-Cu(CH₃COO)₂ composite was dispersed in 50 mL water in a 100 mL two
127 necked round bottom flask and 10 mL aqueous solution of NaBH₄ (134 mg, 3.54 mmol) was
128 then added slowly over 15 min in nitrogen environment under constant stirring condition. The
129 reaction started immediately and the colour changed from blue to black, due to conversion of
130 Cu(II) into Cu⁰-nanoparticles. The black solid mass was recovered and washed with distilled
131 water for several times and then dried in a desiccator for 12 h. The sample thus prepared was
132 designated as Cu⁰-Mont.

133 **2.3. General procedure for the one-pot synthesis of propargylamines**

134 Aldehyde (1 mmol), amine (1 mmol), alkyne (1.2 mmol), 20 mg catalyst and 5 mL
135 toluene were taken in a 25 mL round bottom flask and reaction mixture was refluxed at 110
136 °C for stipulated time period. The progress of the reactions was monitored by TLC. After
137 completion of the reaction, solid catalyst was separated from the mixture by filtered through
138 sintered funnel (G-3) and the solvent was removed under low pressure in a rotavapour. The
139 recovered catalyst was washed with acetone (30 mL), dried in a desiccator and stored for
140 another consecutive reaction run. The crude product obtained was then purified by silica gel
141 column chromatography using ethyl acetate and hexane as eluents. The products were

142 characterized by (^1H , ^{13}C) NMR and mass spectrometry and all gave satisfactory results
143 [supporting information].

144 **3. Results and Discussion**

145 **3.1. Characterization of Support**

146 The naturally occurring Montmorillonite is considered as cheap, robust, easily available
147 and environmentally benign catalysts and catalyst supports.^{15a-f} The purified Montmorillonite
148 was modified with mineral acids treatment under controlled conditions in order to generate
149 high surface area and porous matrix. The characterization of modified Montmorillonite (AT-
150 Mont.) was thoroughly carried out with the help of different sophisticated analytical
151 instruments like Powder-XRD, FTIR, N_2 adsorption-desorption, SEM, ^{29}Si and ^{27}Al MAS-
152 NMR studies and are well documented in our earlier reports.^{15a-f} The parent Montmorillonite
153 (Parent Mont.) is 2 : 1 layered dioctahedral aluminosilicate and consists of two tetrahedral
154 silicate sheets which are bonded to either side of an octahedral aluminate sheet having basal
155 reflection at $7.06^\circ 2\theta$ corresponding to a basal spacing of 12.5 \AA .¹⁷ The powder XRD reveals
156 that after 1 h acid activation, the layered structure is disrupted and becomes amorphous
157 high silica containing matrix [supporting information]. During acid activation, the surface
158 area (upto $422 \text{ m}^2/\text{g}$) (Table 1) as well as pore volume ($\sim 0.6 \text{ cm}^3/\text{g}$) are increased due to the
159 leaching of Al from the octahedral sites of the Montmorillonite matrix, which also introduced
160 permanent porosity on the clay surface. The clay mineral matrix contained micro- ($< 2 \text{ nm}$)
161 and mesopores (2-50 nm) with average pore diameters $\sim 4.28 \text{ nm}$ and also the differential
162 volumes versus pore diameter plot, i.e. BJH plot indicated relatively narrow pore size
163 distributions and these nano range pores were advantageously utilized for the *in situ* synthesis
164 of various metal nanoparticles as reported by us recently.^{15a-f} The shape of N_2 adsorption-
165 desorption isotherm [Fig. 1] was of the type-IV with a H3 hysteresis loop at $P/P_0 \sim 0.4-0.9$,
166 indicating mesoporous solid. The FTIR, ^{29}Si and ^{27}Al MAS-NMR measurements and SEM-
167 EDX studies also confirmed that during acid activation, nano range pores are formed on the
168 surface of clay mineral matrix due to Al leaching and predominant amounts of Si compared
169 to Al were present on the surface [supporting information].^{15a-f}

170 **3.2. Characterization of Cu^0 -nanoparticles**

171 The evidence of formation of Cu^0 -nanoparticles (Cu^0 -Mont.) was obtained from
172 powder XRD analysis. The Fig. 2 shows three broad peaks of 2θ values 43.3 , 50.3 and 74.1°
173 which are assigned to the (111), (200) and (220) indices of fcc lattice of metallic Cu. The
174 XRD peaks for any other oxidation states of Cu were not observed, that could be attributed to
175 the presence of Cu only in zero oxidation state.

176 The TEM image [Fig. 3] of nanoparticles composites showed that dispersed Cu⁰-
177 nanoparticles were formed in the micro- and mesopores of AT-Mont. The supported Cu⁰-
178 nanoparticles were spherical in shape, well separated from each other and with sizes of below
179 10 nm. From TEM study, it was also observed that, some of the Cu⁰-nanoparticles were
180 found to be larger than the pore size of the support which may be due to the presence of Cu⁰-
181 nanoparticles on the outer surface of the support rather than inside the pores. The HRTEM
182 image [Fig. 3(inset)] of single Cu⁰-nanoparticles showed the reticular lattice planes inside the
183 nanoparticles and these planes are continuously extended to the whole particle without any
184 stacking faults or twins, indicating the single crystalline nature.

185 SEM-EDX analysis also substantiated the formation of Cu⁰-nanoparticles on the well-
186 tuned pores of the AT-Mont. Furthermore, EDX analysis indicates that Cu is present on the
187 surface of modified Montmorillonite along with other elements of clay [supporting
188 information].

189 Although, the encapsulation of the Cu⁰-nanoparticles into the nanopores of the
190 modified clay mineral has changed some of the textural parameters of the materials but from
191 the Fig. 4, it is observed that Cu⁰-Mont. exhibits similar type of isotherm and hysteresis loop
192 with that of AT-Mont. This reveals that the highly ordered porous structure of clay is still
193 maintained even after the encapsulation of Cu⁰-nanoparticles. The appreciable decrease of the
194 specific surface area and the specific pore volume after supporting Cu⁰-nanoparticles (Table
195 1) might be due to clogging of some pores by Cu⁰-nanoparticles. In addition, the presence of
196 Cu⁰-nanoparticles may cause complexities in porosity measurement with nitrogen sorption,
197 because the electrostatic forces between an adsorbate (i.e. nitrogen) and metallic surface may
198 affect the measured values to some extent. However, increase of pore diameter may be due to
199 rupture of some smaller pores to generate bigger ones during the formation of Cu⁰-
200 nanoparticles into the pores.

201 The Cu contents in Cu⁰-Mont. as analyzed by ICP-AES, reveals the presence of 0.05
202 mol % of Cu in the catalyst.

203 3.3. Catalytic activity

204 In order to determine the best reaction condition (i.e. solvent, reaction time etc.) that
205 are required to afford excellent yields of propargylamines, a series of three-component
206 reactions were carried out using benzaldehyde, piperidine and phenylacetylene as the model
207 substrates. After screening a wide range of reactions, we have found that our catalytic system
208 (i.e. Cu⁰-Mont.) is most efficient for the title reaction in toluene as a solvent at refluxing
209 temperature. The reactions required 3 h time for completion. A control experiment under the

210 above conditions but in the presence of only acid activated clay (AT-Mont.) as catalyst was
211 done and gave no trace of product after 24 h. Using optimized reaction conditions, we
212 explored the versatility and limitations of some commercially available aldehydes, secondary
213 amines and alkynes as substrates as well as efficiency of our catalyst for the said three-
214 component coupling to synthesise propargylamines derivatives and the results are
215 summarized in Table 2. Firstly, phenylacetylene and piperidine were allowed to couple with
216 different aromatic aldehydes (e.g. benzaldehyde, 4-methoxybenzaldehyde, 4-
217 chlorobenzaldehyde, 4-methylbenzaldehyde, 3-bromobenzaldehyde, 2-hydroxybenzaldehyde)
218 and give corresponding propargylamines with very good to excellent yields. The substituent
219 of the aldehyde seemed to have pronounced effects both on the reaction time and on the
220 isolated yield. The model reaction, i.e. coupling between benzaldehyde, phenylacetylene and
221 piperidine gives 94% isolated yield (entry 1). In case of aldehydes containing electron
222 donating group e.g. 4-methoxybenzaldehyde, 4-methylbenzaldehyde and 2-
223 hydroxybenzaldehyde, it is observed that they required relatively longer time and give
224 slightly lower yield compare to aldehyde containing electron withdrawing group e.g. 4-
225 chlorobenzaldehyde, 3-bromobenzaldehyde. We have also used aliphatic alkyne i.e. 3-
226 butyne-1-ol and allowed to react with two different iminium ions which is generated *in situ*
227 from benzaldehyde and piperidine (entry 8) and benzaldehyde and morpholine (entry 9), it is
228 found that they formed desired propargylamines with high yield. In an another strategy,
229 compared the synthesis of propargylamines by keeping benzaldehyde and phenylacetylene
230 constant and used different secondary amines such as piperidine, morpholine, diethyl amine.
231 The results obtained from the studies reveal that the aliphatic amine i.e. diethylamine (entry
232 7) shows lower conversion than the cyclic amines i.e. piperidine and morpholine (entries 1
233 and 10). Next, we explored our methodology for the synthesis of symmetrical bis-
234 propargylamines derivatives by coupling of dialkyne, viz. 1,6-heptadiyne with benzaldehyde
235 and piperidine (entry 11) and as expected, the desired product is formed with good isolated
236 yield (85%) but the reactions needed a comparatively longer time i.e. 5 h for completion.

237 In order to show the efficiency as well as the practical applicability of the catalyst
238 (Cu⁰-Mont.), we scaled up the reaction of benzaldehyde to 10 mmol with 10 mmol of
239 piperidine and 13 mmol of phenylacetylene under similar optimised reaction conditions. The
240 reaction proceeds well with 90% desired isolated yield and 100% selectivity at 5 h.

241 3.4. Recyclability of the catalyst

242 For practical applications of heterogeneous catalysts, the level of reusability is a very
243 important factor. The recyclability of our catalyst for the three components coupling reactions

244 were investigated (Table 2) in the coupling of phenylacetylene with benzaldehyde and
245 piperidine (entry 1), 4-chlorobenzaldehyde and piperidine (entry 5) and benzaldehyde and
246 morpholine (entry 10). The catalyst was recovered by simple filtration technique after each
247 experiment. The recovered catalyst was washed with acetone, dried in a desiccator and reused
248 directly with fresh reaction mixture without further purification for the desired coupling
249 products synthesis upto 3rd run. The results (Table 2, entries 1, 5 and 10) showed that in each
250 case the catalyst remain active for several run without significantly loss in efficiency.

251 The recovered catalyst was further investigated through N₂ adsorption-desorption,
252 powder XRD studies and HRTEM analysis. The identical shape of the isotherms and the
253 hysteresis loop reveal that the characteristics of the catalysts are retained even after
254 successive reactions [supporting information]. The specific surface areas of the recovered
255 catalysts decrease compared to 299 m²/g of freshly prepared catalyst (Table 1). The decrease
256 of surface area of the recovered catalysts after each reaction may be due to the blockage of
257 pores by the reactant molecules. In the HRTEM analysis of recovered Cu⁰-Mont. (after 3rd
258 run), it is found that a few particles aggregate, but the sizes are still below 10 nm [Fig. 5]. In
259 the powder XRD of recovered catalyst, the appearance of low intense broad peaks at around
260 2θ values 36 and 54° along with other characteristic peaks of metallic Cu indicates the
261 formation of small amount of CuO after 1st run of reaction [supporting information].¹⁸
262 However, the efficiency of the recovered catalyst was not affected much though a fraction of
263 Cu(0) is converted to CuO. This may be, because, the Cu(II) is also known for exhibiting
264 high alkynophilicity. These experimental results are adequate enough to establish the
265 robustness character of the catalyst and also proof that the reactions undergo in a
266 heterogeneous process.

267 A tentative reaction mechanism for the three components (A³ coupling) synthesis of
268 propargylamines catalyzed by Cu⁰-nanoparticles under heterogeneous conditions is proposed.
269 The tentative mechanistic scheme is pictorially illustrated in Scheme 1. It is proposed that, in
270 the first step, terminal alkyne is coordinated to Cu⁰-nanoparticles supported on AT-Mont.,
271 which activates the C–H bond. As a result, corresponding copper-alkylidene complex is
272 formed on the surface of the AT-Mont. This is a very favourable step because Cu metal is
273 well known to exhibit high alkynophilicity for terminal alkynes.^{12a,15a} In the second step, the
274 addition of copper-alkylidene complex to the iminium ion generated *in situ* from the reaction
275 between the aldehyde and the amine, to give the desired product and the catalyst is
276 regenerated. The theoretical by-product formed from the reaction is only water. The
277 regenerated catalyst continues the catalytic cycles till the completion of the reaction. The

278 drastic reduction in catalyst amount requirement as well as reaction time in these reactions
279 are possibly due to the presence of highly active Cu⁰-nanoparticles as catalyst. The presence
280 of robust and high surface area (422 m²/g) modified Montmorillonite as support for Cu⁰-
281 nanoparticles also might have a beneficial effect on the rate and selectivity of the reaction.

282 **4. Conclusion**

283 The nanoporous modified Montmorillonite was found to be excellent eco-friendly
284 support material for the *in situ* synthesis of Cu⁰-nanoparticles. The Cu⁰-nanoparticles were
285 spherical in shape and size in the range 0-10 nm. These nanoparticles demonstrated high
286 catalytic activity in promoting the three-component coupling of aldehyde, amine and alkyne
287 *via* C-H alkyne-activation to synthesize propargylamines with excellent yields and selectivity
288 under mild reaction conditions without requiring any additives or inert atmosphere. Further,
289 the nanocatalysts were reused for new batch of reactions without significantly loss of their
290 activity under the similar condition. The operational simplicity, robustness of the catalyst as
291 well as utilization of environmentally benign indigenous materials as catalyst support and use
292 of mild reaction condition, make it attractive for the large scale synthesis of biologically
293 active propargylamine molecules.

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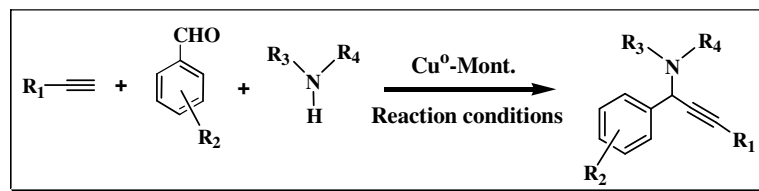
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Table 1: Surface properties of different Montmorillonite based support/catalysts.

Samples	Surface properties of support/catalysts				
	Specific surface area (m ² /g)	Average pore diameter (nm)	BJH pore size distribution (nm)	Specific pore volume (cm ³ /g)	
AT-Mont.	422	4.28	3.77	0.58	
Cu ⁰ -Mont.	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center; margin-right: 10px;"> ↓ Catalyst After run </div> <div style="text-align: center; margin-right: 10px;"> Fresh → </div> <div style="border-bottom: 1px solid black; width: 100px;"></div> </div>	299	5.18	3.81	0.48
	1	255	6.43	3.90	0.38
	2	210	7.25	4.27	0.32
	3	192	8.53	3.89	0.30

Table 2: Cu⁰-nanoparticles catalyst A³ coupling reaction of aldehyde, amine and alkyne.

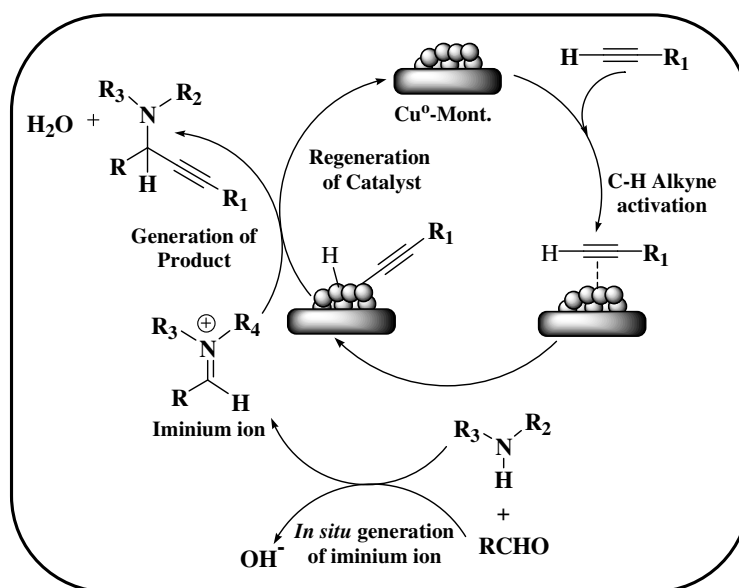
Entry	Alkyne	Aldehyde	Amine	Product	Time (h)	Yield* (%)
1					3	94 ^a
						90 ^b
						88 ^c
2					5	89
3					5	87
4					3	92
5					3	90 ^a
						88 ^b
						85 ^c
6					5	87
7					3	82
8					3	87

9		3	89
10		3	90 ^a 87 ^b 84 ^c
11		5	85

Reaction conditions: Aldehyde (1 mmol), amine (1 mmol), alkyne (1.2 mmol), 20 mg Cu⁰-Mont. (0.05 mol %), solvent: toluene, temperature: 110 °C.

Yields are given for isolated products;

*The reaction products were free from copper as checked by analytical method followed from Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis; Revised by G. Svehla, Fifth Edition, 1979, Longman Group Limited, London, Page No.: 215-217. Methodology: 100 mg of each of the reaction products (from entries 1 or 2) were dissolved in 10 mL of medium concentrated HNO₃ (8 M). The solution was diluted by adding 10 mL of distilled water followed by passing H₂S gas through the solution for a period of 5 minutes. No black color precipitate was observed. Hence, reaction products were free from Cu. The detection concentration limit is: 1 in 5 x 10⁶.



Scheme 1. Tentative reaction mechanism of A³ coupling reaction.

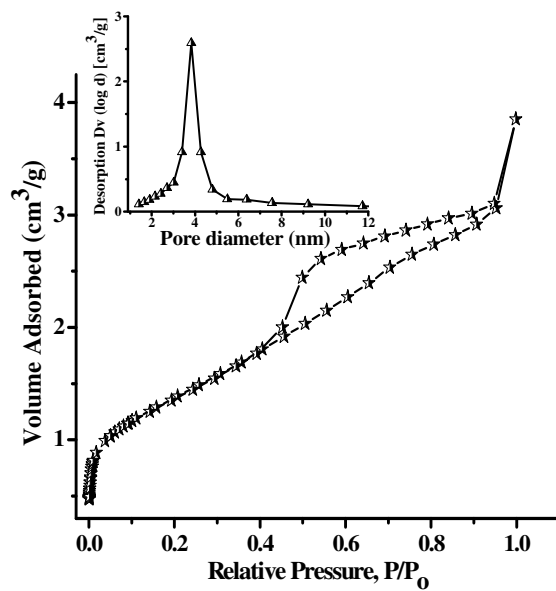


Fig. 1. N₂ adsorption–desorption isotherm and BJH pore size distribution curve (inset) of AT-Mont.

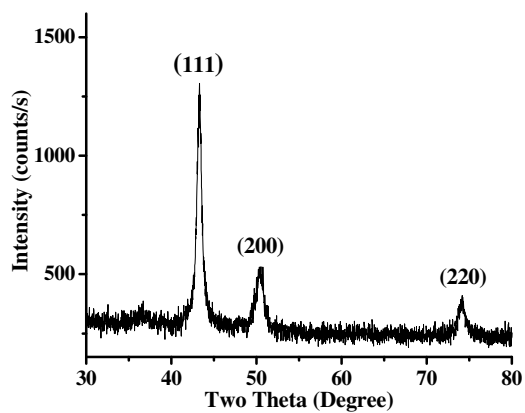


Fig. 2. Powder XRD pattern of Cu⁰-Mont.

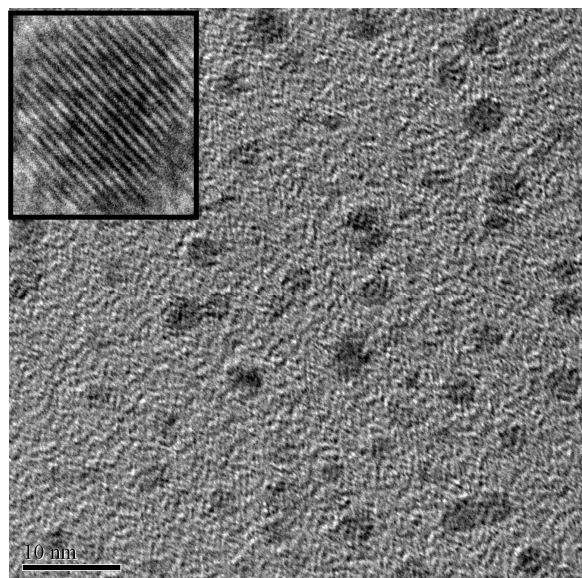


Fig. 3. TEM and HRTEM (inset) images of Cu⁰-nanoparticles.

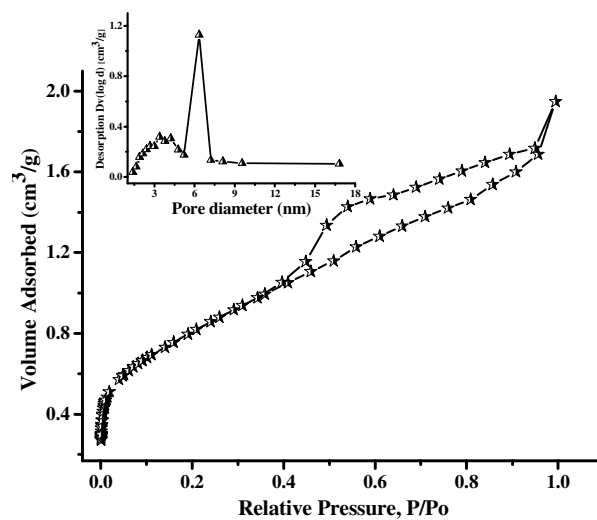


Fig. 4. N₂ adsorption/desorption isotherm and BJH pore size distribution curve (inset) of Cu⁰-Mont.

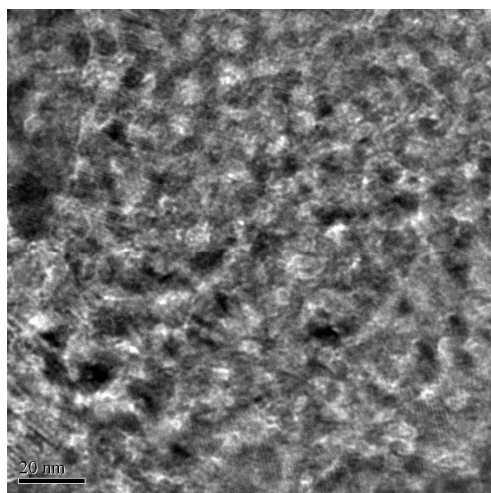


Fig. 5. HRTEM image of recovered Cu⁰-Mont. after 3rd run.

Efficient Three-Components Coupling Reactions Catalyzed by Cu⁰-nanoparticles stabilized on Modified Montmorillonite Clay

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Graphical Abstract

In situ generation of Cu⁰-nanoparticles into the nanopores of environmentally benign modified Montmorillonite clay and their catalytic performance in three components (A³) coupling reactions of aldehyde, amine and alkyne to synthesize propargylamines with excellent yield and selectivity.

