

Copper(II) ion-exchanged montmorillonite as catalyst for the direct addition of N–H bond to CC triple bond

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Abstract

An efficient synthesis of phenyl-(1-phenylethylidene)amine using copper-exchanged montmorillonite clay (Cu K-10) is demonstrated. The catalyst was characterized using UV–vis, XRD, BET surface area measurements, pyridine adsorption etc. The XRD and surface area measurement show that the structural characteristics of the support montmorillonite K-10 (K-10) are preserved after Cu exchange. The hydroamination of phenyl acetylene with aniline was carried out in toluene under reflux condition in N₂ atmosphere at 393 K. The reaction is highly regio-selective for only Markovnikoff's addition of amine to CC multiple bond and proceeded smoothly to completion. The reaction conditions were optimized to obtain complete conversion with respect to phenyl acetylene. Reaction data showed that the activity of the catalyst in hydroamination reaction is greater at higher reaction temperatures and nonpolar solvents and N₂ pressure promotes the reaction drastically.

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1. Introduction

Among the addition reactions, the addition of N–H bonds across the CC multiple bonds known as hydroamination is of considerable interest in organic synthesis [1]. It is thermodynamically feasible reaction where amines can be obtained directly without any by-product. Hydroamination is used to synthesize numerous classes of organo-nitrogen molecules such as alkylated amines, enamines or imines that are used as chemical intermediates in the area of natural products, pharmaceuticals, fine chemicals, dyes, polymers and surfactants [2].

As a result of extensive research since the last 4 decades, catalytic route for hydroamination of smaller molecules like ethylene has been developed but a breakthrough in catalytic activity is not achieved. Although considerable progress has been made using metal complex catalysts under homogeneous conditions [1,2], an efficient heterogeneous

and highly selective catalytic route is yet to be achieved. Some palladium(II) and late transition metal complexes have been investigated as homogeneous catalysts for hydroamination reactions [3–8]. Efforts have also been made to immobilize some of the palladium complexes [9] and use them as heterogeneous catalysts. Muller et al. in their review “metal-initiated amination of alkenes and alkynes” [2] have reviewed the entire literature on amination of alkenes and alkynes up to the year 1998. Lanthanide complexes and rare earth metal catalysts have shown activities in the amination in particular in the regioselective cyclization of aminoalkenes and alkynes [10,11]. However, the rates of amination being poor (TOF <140 h⁻¹), its cost and handling makes these systems less attractive for commercial applications. There are few studies on acidic zeolite (H-β, ZSM-5, H-Mordenite, H-Y, H-Clinoptilolite and H-Erionite) catalyzed hydroamination of olefins at high temperatures and pressures [12,13]. Recently, some attempts have been made to develop the heterogeneous catalysts such as transition metal incorporated H-β zeolite for hydroamination reactions [14,15].

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This work aims at finding efficient and selective solid catalyst for hydroamination reactions of unsaturated compounds utilizing transition metal ions incorporated in montmorillonite K-10. Montmorillonite clays have a layered structure and have attracted considerable research interest as an environmentally benign and reusable catalyst for a variety of reactions [16]. Clay has an interlamellar water layer containing dissolved cations sandwiched between extended aluminosilicate sheets where two external tetrahedral silica layers surround internal octahedral alumina layer in a tetrahedral octahedral tetrahedral (TOT) structure. By replacing the interlayer ions with high charge density cations like Al^{3+} , Zn^{2+} and Fe^{2+} acidity can be imparted in the clay and can be utilized for a broad range of organic transformations [17–19]. In this current paper, we have utilized this property of clay and have synthesized Cu^{2+} exchanged K-10 montmorillonite clay and used it as a green, inexpensive and efficient catalyst for the intermolecular hydroamination of alkynes.

2. Experimental

2.1. Materials

Montmorillonite K-10 was purchased from Fluka AG, Switzerland. Its wt.% composition was $\text{SiO}_2 = 70$, $\text{Al}_2\text{O}_3 = 15$, $\text{Fe}_2\text{O}_3 = 1.5$, $\text{CaO} = 2.5$, $\text{MgO} = 3$, $\text{Na}_2\text{O} = 0.5$, $\text{K}_2\text{O} = 1.5$, and $\text{H}_2\text{O} = 6$ and bulk density = 300 ± 30 g/l. Phenyl acetylene was purchased from Aldrich. Aniline, $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ and toluene were purchased from S.D Fine Chem Ltd., Mumbai. All the chemicals were used as received. Toluene used in the reaction was distilled over sodium wire before use.

2.2. Synthesis

Cu K-10 was prepared by slurring K-10 (10 g) dried at 373 K overnight with 0.5 M aqueous solution of $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ (50 ml) at 363 K for 8 h and then cooled to room temperature and filtered. This process was repeated to ensure complete copper exchange. The solid obtained was filtered and washed many times with water and dried at 373 K for 12 h and then calcined (RT: 573 K, 3°C min^{-1} ; and then kept at 573 K for 4 h). To study the effect of calcination on the rate of reaction the catalysts was also calcined at different temperatures (373–573 K).

2.3. Characterization of catalysts

The electronic spectra of the catalyst were taken on a Shimadzu UV–vis scanning spectrophotometer (Model 2101 PC). Powder X-ray diffraction patterns of the catalysts were recorded using a Rigaku (Model D/MAXIII VC, Japan), setup with Cu $\text{K}\alpha$ radiation and a graphite monochromatic with scan speed 5°min^{-1} and scanning in the 2θ range from 5 to 50 2θ . Silicon was used to calibrate the instrument. The

Brönsted and Lewis acid sites in Cu K-10 were estimated by adsorption of probe molecule, viz. pyridine using Shimadzu SSU-8000 in the DRIFT (diffusive reflectance IR Fourier transform) mode. In a typical experiment, a 20 mg of the sample was placed in a specially designed cell. The sample was heated in situ from room temperature (5°C min^{-1}) to 573 K under N_2 flow (flow rate 40 ml min^{-1}) for 3 h followed by cooling to 373 K. Pyridine vapors were then introduced in two parts of 10 μl each into the cell under N_2 flow. Spectra were recorded after outgassing at different temperatures (373–573 K) for 30 min. The copper content of the samples was measured by atomic absorption spectrometer (AAS-Hitachi Model Z-8000). Surface area of the catalysts was determined by Omnisorb 100 CX (Coulter, USA).

2.4. Catalytic activity measurements

Experiments were carried out in a two-necked round bottom flask fitted with a water condenser connected to a balloon filled with N_2 and kept in a thermostatic oil bath at a temperature of 393 K at atmospheric pressure. Reaction mixture containing phenyl acetylene (0.885 g), aniline (1.615 g), toluene (6 ml) and catalyst (0.125 g, catalyst calcined at 573 K) was placed in the flask. The flask was then flushed twice with N_2 before it was finally connected to balloon filled with N_2 . The reaction was initiated by stirring the reaction mixture with a magnetic needle.

To study the effect of N_2 pressure, the experiments were carried out in a 50 ml Parr autoclave under N_2 pressure. In a typical experiment, catalyst (calcined at 573 K) and reaction mixture containing known amounts of the reactants was placed into the autoclave. The autoclave was then pressurized with N_2 up to 100 psig after flushing twice with N_2 and was then heated to 393 K and kept at that temperature under constant stirring. Samples were withdrawn at regular intervals of time were analyzed by gas chromatography (Shimadzu 14B) equipped with a cross linked 5% diphenyl–95% dimethylpolysiloxane capillary column (30 m) and a flame ionization detector and the identity of the product was confirmed by GC–MS (Shimadzu GCMS QP 5000) equipped with an identical column and a mass selective detector.

3. Results and discussion

3.1. Characterization

The XRD profile of K-10 (Fig. 1a) showed a layered structure with a basal spacing (d_{001}) of 3.34 Å. After treatment of K-10 with $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ the XRD studies of Cu K-10 (Fig. 1b) showed that the layered structure is retained and the basal spacing of (d_{001}) was estimated to be 3.35 Å, which is comparable to that of the parent K-10. The XRD of Cu K-10 catalysts after the reaction (Fig. 1c—Spent catalyst) also retained the layered structure with a basal spacing (d_{001}) of 3.33 Å.

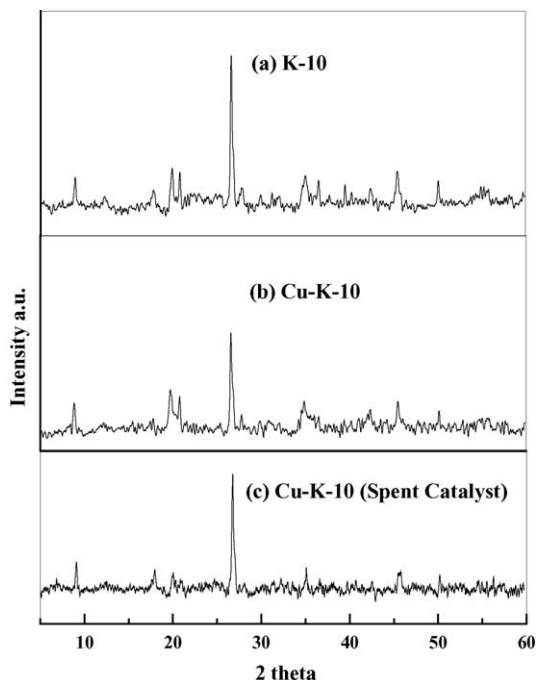


Fig. 1. XRD pattern of (a) K-10 (b) Cu K-10 (c) Cu K-10 spent catalyst.

The diffuse reflectance UV–vis spectrum of K-10 and Cu K-10 is depicted in Fig. 2. K-10 does not have any absorption band above 400 nm. However, Cu K-10 exhibits a strong band with a maximum at 549 nm which is attributed to the d–d transitions of Cu(II). Adsorption of pyridine on the surface of catalysts is one of the most frequently used methods for determination of surface acidity. The use of IR

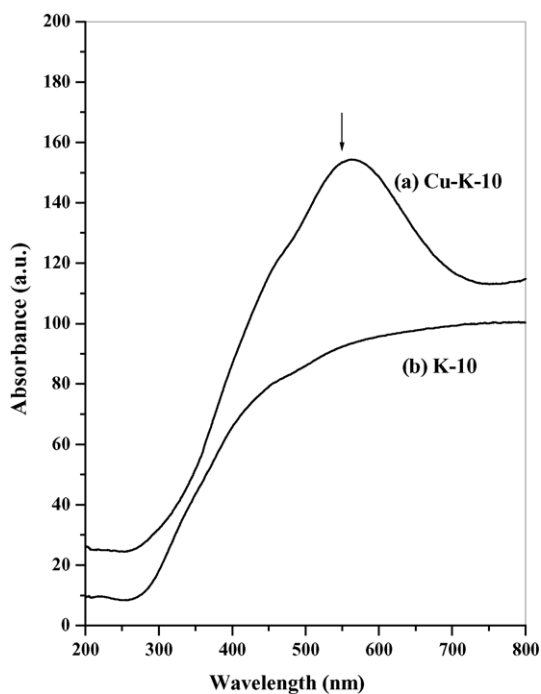


Fig. 2. Electronic spectra of (a) K-10 (b) Cu K-10.

spectroscopy to detect adsorbed pyridine enables us to distinguish different acid sites. The presence of acidity (Brønsted and Lewis acidity) was determined for K-10 and Cu K-10 using pyridine adsorption in situ FT-IR Spectroscopy (Fig. 3). The catalyst showed Brønsted (B) and Lewis (L) acidity at 1541 cm^{-1} and 1450 cm^{-1} , respectively that is assigned to pyridine molecule interacting with Brønsted and Lewis acid sites of the catalyst. Brønsted acidity decreased after Cu exchange but retained a small amount as shown in Fig. 3. An increase in the absorption band at 1450 cm^{-1} (Lewis acidity) is observed on incorporating copper ions. It is shown in earlier reports that Brønsted acid sites in the vicinity of Lewis acidic metal center (active sites) act as co-catalyst [14,20].

3.2. Hydroamination of phenyl acetylene

For exploring the potential of this catalyst, the hydroamination of phenyl acetylene was carried out in toluene under reflux condition and the reaction conditions were optimized to obtain complete substrate conversion. The hydroamination (direct addition of N–H bond to CC multiple bond) of phenyl acetylene with aniline gave only the preferred Markovnikoff's addition product phenyl-(1-phenylethylidene)amine (Fig. 4). The effect of catalyst,

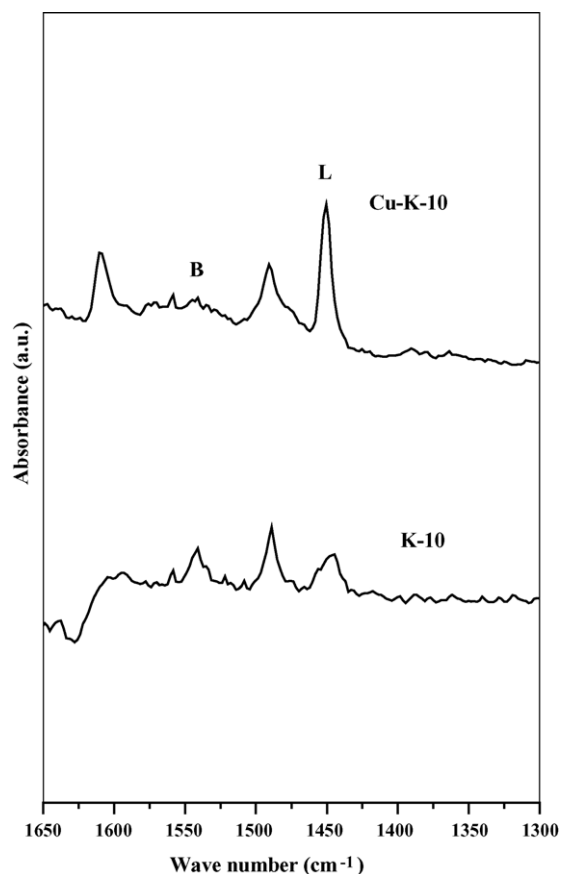


Fig. 3. FTIR Pyridine adsorption of (a) K-10 (b) Cu K-10.

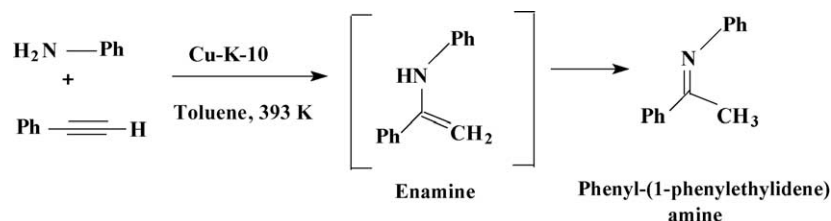


Fig. 4. Reaction scheme for hydroamination of phenyl acetylene with aniline.

substrate concentrations, solvent amount, solvent concentrations and temperature on hydroamination of phenyl acetylene with aniline over Cu K-10 was investigated. The following observations were noted when studies were carried out at the following reaction conditions:

- (i) The catalyst amount was varied between 0.065 and 0.25 g by keeping the temperature (393 K), amount of solvent (6 ml) and mole ratio of phenyl acetylene and aniline (1:2) constant. A linear increase in the rate of phenyl acetylene conversion with time is observed over a period of 5 h on increasing the catalyst amount from 0.065 to 0.25 g (Fig. 5). After 5 h with the catalysts amount of 0.25 g, a steady state is observed (even though the initial rate was high) while with catalysts amount in the range of 0.065–0.125 g further increase in conversion is observed with time.
- (ii) Phenyl acetylene to aniline mole ratio was varied from 1:1 to 1:3, by keeping the temperature (393 K), amount

of solvent (6 ml) and catalyst (0.125 g) constant. On increasing the concentration of aniline it is observed that (Fig. 6) after 9 h the conversion for phenyl acetylene for the entire ratio is same. An initial increase in the conversion is observed on increasing the amount of aniline from 1:1 to 1:2. However, further increase in the amount of aniline has a detrimental effect on the rate of reaction.

- (iii) Temperature was varied between 373 and 413 K, by keeping amount of solvent (6 ml), catalyst (0.125 g) and ratio of phenyl acetylene and aniline (1:2) constant (Fig. 7). On increasing the temperature from 373 to 413 K a linear increase in the conversion was observed. A maximum conversion of 94% with 100% selectivity was observed for a temperature of 413 K over a period of 9 h. However, on continuing the reaction for longer time complete conversion with respect to phenyl acetylene was observed.

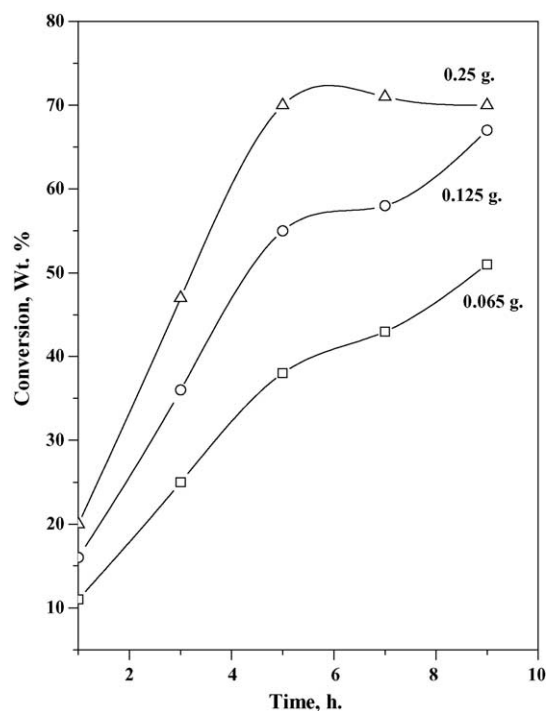


Fig. 5. Effect of catalyst concentration on the hydroamination of phenyl acetylene with aniline. Reaction conditions: phenyl acetylene and aniline molar ratio 1:2, temperature = 393 K and toluene = 6 ml.

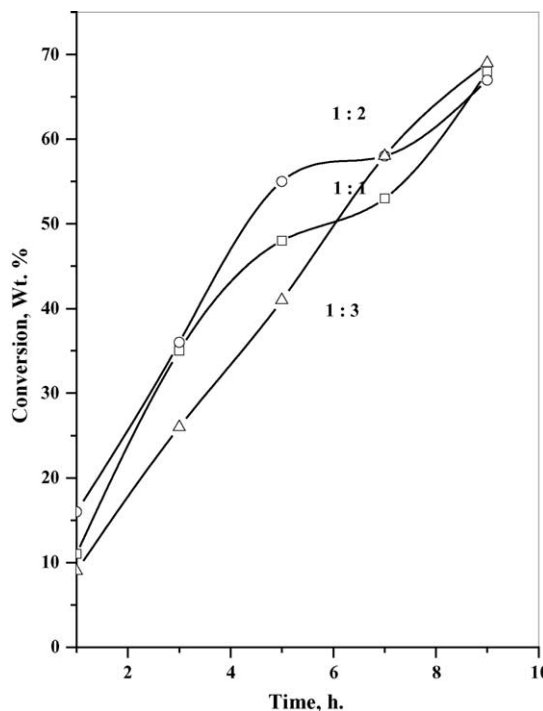


Fig. 6. Effect of phenyl acetylene/aniline mole ratio on the hydroamination of phenyl acetylene with aniline. Reaction conditions: temperature = 393 K, catalyst = 0.125 g and toluene = 6 ml.

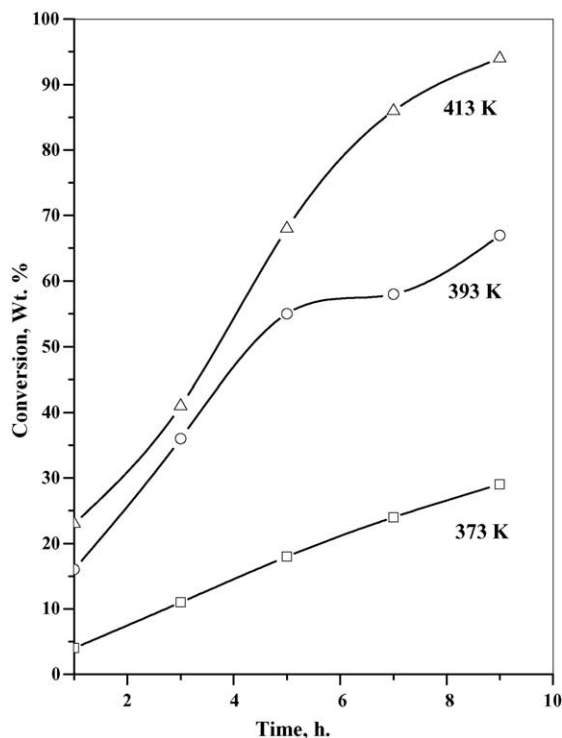


Fig. 7. Effect of temperature variation on hydroamination reaction. Reaction conditions: phenyl acetylene and aniline molar ratio 1:2, catalyst = 0.125 g and toluene = 6 ml.

- (iv) By keeping amount of solvent (6 ml), temperature (393 K), catalyst (0.125 g) and ratio of phenyl acetylene and aniline (1:2) constant different solvents were used and their effect on the conversion was studied (Fig. 8). The conversion increased in the following order tetrahydrofuran < acetonitrile < benzene < toluene. The polar solvents retard the rate of reaction and this could be because of strong adsorption of the same on the support, which hinders the availability of reactants for the reaction. Among the various solvents used, toluene was found to be the best solvent.
- (v) Amount of toluene was varied in between 6 and 0 ml. It is observed that reaction takes place even without toluene but it is also observed that the reaction mixture becomes very viscous as the reaction proceeds. On increasing the amount of toluene it is observed that the conversion decreases (Fig. 9). This could be because of the lowering of the concentration of the reactants in presence of toluene.
- (vi) Reactions were also carried out with catalysts calcined at temperatures in the range of 373–573 K, keeping the amount of copper constant in the catalyst. However, it was observed that calcining the catalysts at 573 K did not have any effect in the reaction rate (Table 1, entry 2–4). Similar observation was also made by Muller and co-workers [15]. Hence, the catalyst can be used for the reaction after drying at 373 K.

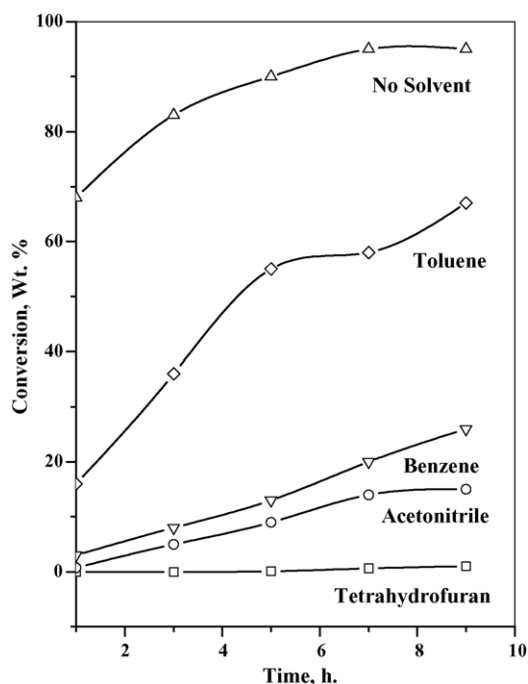


Fig. 8. Effect of solvent on the hydroamination of phenyl acetylene with aniline. Reaction conditions: phenyl acetylene and aniline molar ratio 1:2, catalyst = 0.125 g, temperature = 393 K, and solvent = 6 ml.

- (vii) Effect of N_2 pressure on the reaction rate was also studied by carrying out the reaction in a Parr Autoclave. It was observed that under atmospheric pressure the reaction took 10 h for complete conversion,

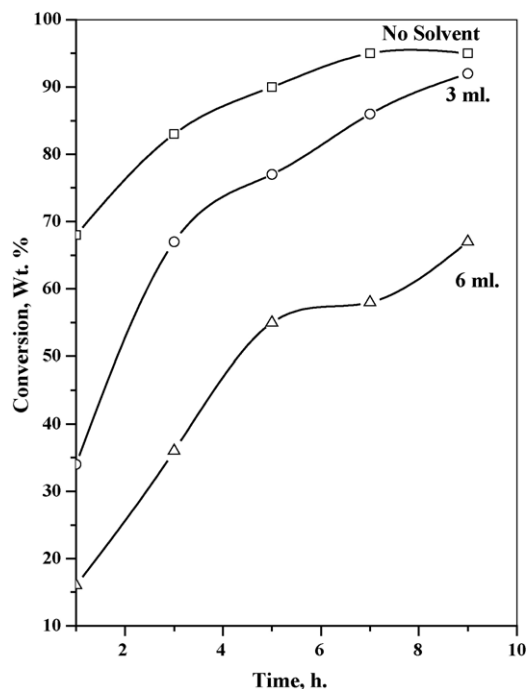


Fig. 9. Effect of amount of toluene on the hydroamination of phenyl acetylene with aniline. Reaction conditions: phenyl acetylene and aniline molar ratio 1:2, catalyst = 0.125 g and temperature = 393 K.

Table 1
Catalytic activity at different calcination temperature and surface area of catalysts

No	Catalyst	Calcination temperature of catalyst (K)	Copper content (mmol/g)	Surface area (m ² /g)	Conversion (%)
1.	K-10	573	Nil	232	1
2.	Cu K-10	573	0.9	226	36
3.	Cu K-10	473	0.9	–	35
4.	Cu K-10	373	0.9	–	35.4

Reaction conditions: phenyl acetylene and aniline molar ratio 1:2, temperature = 393 K, catalyst = 0.125 g, time = 3 h and toluene = 6 ml.

but on applying a pressure of 4 bar, complete substrate conversion was observed over a period of 5 h. Hence, pressure has a drastic effect on the rate of reaction.

- (viii) Activity of a particular metal also depends on the acidity of the metal cation. As Cu²⁺ is moderately acidic it gives very high activity for hydroamination compared to other metals. Based on the experimental evidence in literature [15] and our previous report [19], the mechanism speculated is the nucleophilic addition of amine to the alkyne coordinated to the Cu²⁺ to form the 2-ammonioalkenyl complex and further the protonation of the carbon attached to the copper to release the product. The copper substrate complex is neither too unstable nor too stable to undergo further reaction.

4. Conclusions

A catalyst Cu²⁺ ion exchanged montmorillonite clay is prepared. This catalyst is tested for the hydroamination of phenyl acetylene with aniline in toluene. Only Markovnikoff's addition product was formed and the reaction was very facile which proceeded smoothly to completion. Compared to other solvents used, toluene is found to be a suitable solvent. However, rate of reaction is more when the reaction is carried out with lesser amount of solvent and in the absence of solvent. The rate of hydroamination reaction is greater at higher reaction temperatures and pressure promotes the reaction drastically. Cu²⁺ exchanged K-10 montmorillonite clay proved to be a green, inexpensive and efficient catalyst for the intermolecular hydroamination of alkynes.

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