Intermolecular hydroamination of alkynes catalyzed by zinc-exchanged montmorillonite clay

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Abstract

Intermolecular hydroamination of phenyl acetylene (PhAc) by aniline to give phenyl-(1-phenylethylidene) amine has been investigated using Zn^{2+} exchanged K-10 montmorillonite clay (hereafter Zn/K-10) catalysts. Under optimized reaction conditions, aniline to PhAc mole ratio 2, toluene solvent, catalyst Zn/K-10 (0.5 g) and at 130 °C gave 77 wt.% conversion of PhAC after 20 h. The activities of Zn/K-10, Zn/H-beta and Zn/silica having same amount of Zn^{2+} were compared. Zn/H-beta and Zn/K-10 showed nearly the same activity at the end of 10 h and others followed in the order Zn/silica, H-beta, K-10 and silica. The role played by Lewis and Brönsted acidities of the catalysts in influencing the catalytic activity for hydroamination reaction has been discussed. It is suggested that Brönsted acidity acts as a co-catalyst for Lewis acidic metal center. Zn/K-10 is the inexpensive but efficient catalyst for intermolecular hydroamination of alkynes, which can be utilized as an alternative to Zn/H-beta catalyst.
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1. Introduction

The synthesis of compounds containing carbon–nitrogen bonds is of fundamental interest in organic chemistry [1,2]. The direct addition of amines to C–C double and triple bonds known as hydroamination, offers the most attractive route to prepare numerous class of organo-nitrogen molecules such as alkylated amines, enamines and imines. These compounds are of significant industrial importance as chemical intermediates in the synthesis of natural products, pharmaceuticals, dyes, fine chemicals, polymers and surfactants [3].

The industry produces amines following various synthetic routes especially the reaction between ammonia with alcohol [4]. These methods suffer from drawbacks such as by-product formation as well as poor product selectivity. Condensation of ketones with amines is the textbook route to prepare enamines

and imines but this reaction produces water as a by-product and hence limits its use in the domino reactions such as direct nucleophilic addition of organometallic reagents. Also aromatic ketones react slowly compared to aliphatic ketones and methyl ketones are sensitive to aldol type side reactions [5]. Hence, synthesis of imines from acetophenone always ends up in unsatisfactory yields [6,7].

Hydroamination reaction merges perfect atom economy with thermodynamic feasibility. However, this reaction has a considerable kinetic barrier and hence the use of catalyst is a desired option. There are reports in the literature on hydroamination reactions, wherein the intermolecular hydroamination of alkynes has been carried out with salts of Hg and Tl and alkali metal catalysts [3]. Homogeneous catalysts consisting complexes of early transition and late transition metals, lanthanides, and actinides have been developed to promote the hydroamination reactions [8,9]. These homogeneous catalysts are least preferred by the industry since they generate problems such as environmental pollution, handling, safety, corrosion and tedious work up.

Heterogeneous catalysts, mainly zeolites in their H-form have been used in the hydroamination reactions but mostly restricted to the reaction between ammonia and C_2–C_4 alkenes [10–12]. These reactions have been carried out at high temperatures and pressures, which suffered from low product yields [13]. Till now, only one process-synthesis of *t*-butyl amine using ammonia and isobutene catalyzed by H-ZSM-5 has been commercialized [14]. Attempts have been made recently to develop heterogeneous catalyst consisting of transition metal ion incorporated zeolite beta catalyst for intramolecular hydroamination reactions [15,16].

Aim of our present study is to develop a transition metal exchanged montmorillonite K-10 clay as a catalyst for intermolecular hydroamination reaction of alkynes. K-10 is an inexpensive and non-corrosive acid activated clay, which has been used as an efficient catalyst for wide variety of reactions [17]. It is mesoporous in nature with basal spacing dL between tetrahedral silicate and octahedral aluminate layers may vary between 1 and 5 nm depending on the amount of intercalated water in the interlamellar space. The interlayer cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} contribute to the acidity in montmorillonite clay. Protons, polarizing cations (e.g. Al^{3+}) present in the interlayer region, terminal hydroxyl groups and bridging oxygen atoms present in the layers give rise to Brönsted acidity. The concentration of exchangeable cations (CEC) of montmorillonite clay ranges from 70 to 120 mequiv./100 g of dried clay. These interlayer cations can undergo exchange with cations from external solutions. This property of K-10 has been utilized to prepare zinc ion exchanged catalysts with various concentration of zinc and their catalytic performance in intermolecular hydroamination of phenyl acetylene by aniline has been investigated. The catalytic activity of Zn/K-10 with optimum zinc loading has been compared with Zn/H-beta and Zn/silica. Brönsted and Lewis acidities in these ion exchanged catalysts shown to have a specific role in hydroamination reactions [18–21]. Role of acidity in the formation of phenyl-(1-phenylethylidene) amine in hydroamination reaction has also been discussed.

2. Experimental

2.1. Materials

Montmorillonite K-10 was purchased from Fluka AG, Switzerland. Its wt.% composition was $SiO_2 = 70$, $Al_2O_3 = 15$, $Fe_2O_3 = 1.5$, $CaO = 2.5$, $MgO = 3$, $Na_2O = 0.5$, $K_2O = 1.5$, and $H_2O = 6$ and bulk density = 300 ± 30 g/l. Phenyl acetylene was purchased from Aldrich. Aniline, metal acetates and toluene were purchased from S.D. Fine Chem Ltd., Mumbai. H-beta (Si/Al = 15) was obtained from CPP, NCL Pune. Silica gel was prepared by hydrolysis of tetraethyl orthosilicate (Aldrich) in presence of catalytic amount of con. HNO_3.

2.2. Catalyst preparation

A known amount of K-10 (10 g) was stirred with 0.5 M zinc acetate solution prepared in water (50 ml) at 80 °C for 10 h and then cooled to room temperature and the exchanged clay was separated by filtration. The above procedure was repeated once to ensure maximum zinc exchange. The residue obtained was filtered and washed twice with 100 ml of distilled water. This zinc-exchanged K-10 was dried at 120 °C for 12 h and then calcined (RT–300 °C, 3 °C min^{-1}; for 4 h at 300 °C). The catalysts with varying concentrations of Zn in K-10 were prepared by taking different zinc acetate stock (0.01–0.5 M) solutions, by following the above procedure. Similarly, Zn/H-beta, Zn/silica, Co/K-10, Mn/K-10 and Pd/K-10 catalysts were prepared by exchanging with the pre decided stock solutions of the corresponding metal acetate by following the above procedure. Calcination program followed for Zn/H-beta and Zn/silica was RT–500 °C, 2 °C/min; 4 h at 500 °C. BET surface area of catalysts was determined by Omnisorb 100 CX (Coultier USA). The amount of exchanged metals on supports was determined by atomic absorption spectrophotometer (AAS-Hitachi Model Z-8000) except for Pd (determined by ICP-OES) following the standard procedure.

The Brönsted and Lewis acid sites in zinc-exchanged zeolites was 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 300 °C under N_2 flow (flow rate 40 ml/min) for 3 h followed by cooling to 100 °C. 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 (100–300 °C) for 30 min.

In a typical reaction, the reaction mixture consisting of phenyl acetylene (1.77 g), aniline (3.23 g), toluene (12 ml) and catalyst (0.25 g) placed in a 50 ml round bottom flask which was kept in an oil bath and refluxed (111 °C) under N_2 atmosphere. Toluene was used as a solvent since it prevents metal ion from leaching into the reaction mixture besides having other common advantages of a solvent. Samples were withdrawn at regular intervals of time and analyzed for its contents by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using a capillary column. The authenticity of the product was confirmed by GC–MS and conversion of phenyl acetylene was estimated in weight percentage.

3. Results and discussion

Intermolecular hydroamination of phenyl acetylene by aniline to give phenyl-(1-phenylethylidene) amine (Scheme 1) was chosen as a model reaction for testing the performance of metal exchanged K-10 as a catalyst and com-

enamine intermediate   **phenyl-(1-phenyl ethylidene)amine**
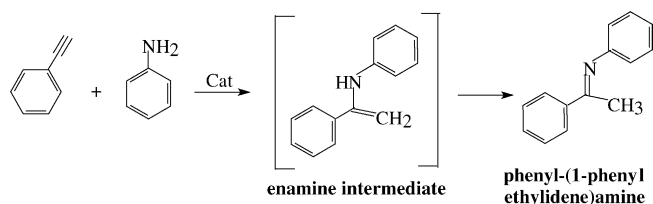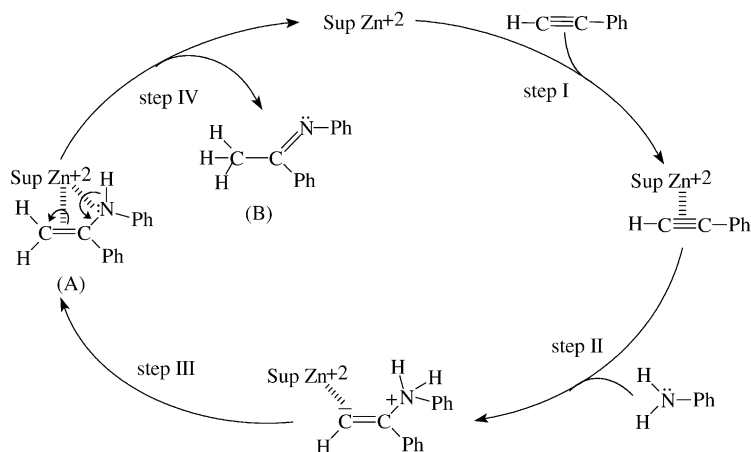
Scheme 1.

paring its performance with other supports H-beta and silica. In the above reaction, enamine is formed as an intermediate, which being unstable undergoes rearrangement to form stable phenyl-(1-phenylethylidene) amine. This reaction is highly regioselective and only Markovnicov addition product was formed under the reaction conditions studied.

3.1. Mechanism of hydroamination

Two approaches are possible for transition metal catalyzed hydroamination reactions, which involve primarily the activation of either an amine or an alkyne. Amine activation takes place via oxidative addition of the N−H bond by transition metal in a lower oxidation state. Insertion of alkyne into the metal nitrogen bond results in β-aminoalkenyl metal complex, which further gives final product by reductive elimination. But this approach is least possible for Zn considering its stable solitary +2 oxidation state. Hence the most probable mechanism for hydroamination of PhAc by aniline catalyzed by Zn^{2+} ion exchanged K-10 can be explained via alkyne activation as shown in Scheme 2. PhAc forms a π-coordination complex with the Zn^{2+} ion (step I). This makes the π–electron system more vulnerable to nucleophilic attack of aniline. Hence nucleophilic addition of aniline (Markovnicov addition as shown in step II) results in β-ammonioalkenyl zinc complex. 1,3-Proton shift in β-ammonioalkenyl zinc complex gives enamine (A) as hydroamination product (step III). Enamine being unstable rearranges itself to give stable imine (B) in step IV, while regenerating the catalyst in a cycle.

Table 1

S. no.	Catalyst	Metal acetate concentration (mol/l)	Metal content (mmol/g)	Surface area (m²/g)
1	Zn/K-10	0.5	0.60	177
2	Zn/K-10	0.2	0.51	201
3	Zn/K-10	0.1	0.38	213
4	Zn/K-10	0.05	0.22	224
5	Zn/K-10	0.02	0.10	227
6	Zn/K-10	0.01	0.04	230
7	Zn/silica	0.1	0.37	151
8	Zn/H-beta	0.1	0.38	481
10	Pd/K-10	0.1	0.37	221
12	Co/K-10	0.1	0.39	223
13	Mn/K-10	0.1	0.38	220
14	ZnO	–	–	10
15	Clay		–	232
16	H-beta	–	–	550
17	Silica	–	–	201

3.2. Characterization of catalysts

Amount of zinc and BET surface area of the catalysts are given in Table 1. The increase in metal concentration resulted in decrease in surface area. XRD measurements of parent K-10 and Zn/K-10 catalysts indicated that there was no structural change after Zn-exchange. Pyridine adsorption in situ FT-IR spectroscopy was performed for K-10 and Zn incorporated K-10 catalysts and the spectra recorded after outgassing at 200 °C are represented in Fig. 1. Adsorption of pyridine on the parent K-10 clay resulted in absorption bands at 1540 and 1450 cm^{-1}, which can be assigned to pyridine molecules interacting with Bronsted and Lewis acid sites, respectively. Incorporation of zinc led to an increase in Lewis acidity as shown in Fig. 1. In contrast, there is decrease in concentration of Brönsted acid sites with increase in zinc loading in the range of 0.1–0.6 mmol Zn per gram of K-10.
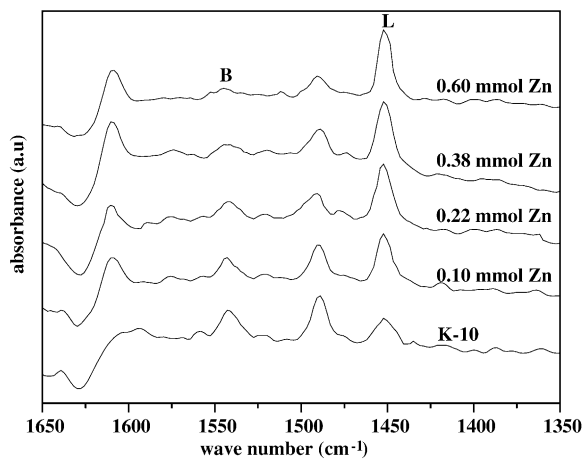

Scheme 2. Proposed mechanism for hydroamination of PhAc by aniline catalyzed by Zn/K-10.

Fig. 1. FT-IR pyridine adsorption of K-10 and Zn/K-10 catalysts for Brönsted (B) and Lewis acid sites (L).

3.3. Catalytic results

In order to find the influence of divalent transition metals exchanged with K-10 catalysts on the intermolecular hydroamination of phenyl acetylene by aniline, the catalysts prepared with different transition metals such as Zn, Pd, Co, Mn were tested and their performance is as shown in Fig. 2. It is seen that Zn/K-10 showed the highest activity with 46% conversion of PhAc and the others followed as Pd/K-10 (12.4%), Co/K-10 (7.2%) and Mn/K-10 (4.8%) after 10 h of reaction. Zinc-exchanged H-beta has been used as a catalyst for hydroamination reaction and H-beta was reported as the best support among zeolites [15]. The catalytic performance of Zn/K-10 has been compared with supports H-beta and silica containing similar zinc concentrations and the results are presented in Fig. 3. The conversion of PhAc after 10 h for Zn/H-beta (47.9%) was marginally higher in
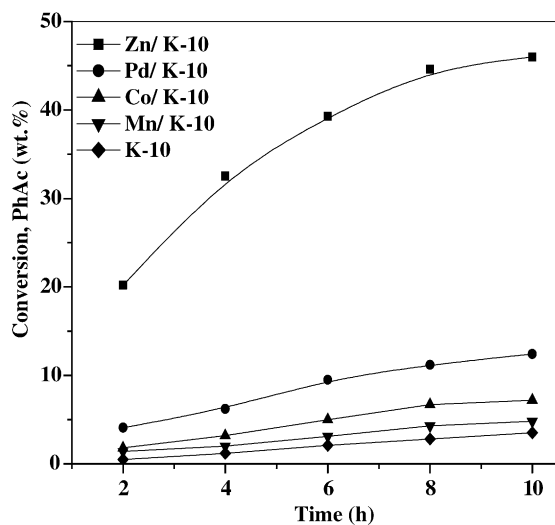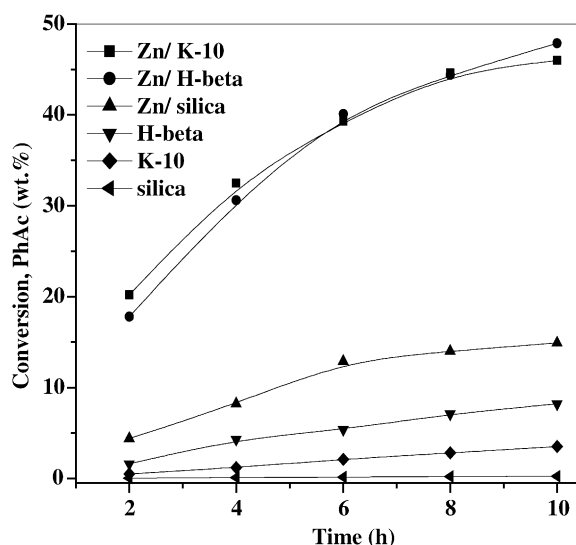

Fig. 3. Effect of support on the catalytic activity in hydroamination of PhAc by aniline. Conditions: temperature = 111 °C, aniline to PhAc mole ratio = 2, catalyst weight = 0.25 g, total reactants weight = 5 g.

comparison with Zn/K-10 (46%) under similar reaction condition, while Zn/silica is at least three times less active than the other two.

The effect of Zn^{2+} concentration on the catalytic activity of the Zn/K-10 was studied with Zn^{2+} concentrations ranging from 0.04 to 0.60 mmol/g and the results are shown in Fig. 4. The conversion of PhAc increased linearly up to 0.22 mmol/g of zinc and further increase has the marginal effect on the catalytic activity. Zn^{2+} is exchanged with interlayer cations as well as the Brönsted acid sites up to a concentration of 0.22 mmol/g. The higher loading results in incorporation of zinc species as ZnO after calcination, which does not contribute to the catalytic activity [22]. This was confirmed by independent experiment (seen in Fig. 4) and the low activity

Fig. 2. Time–PhAc conversion profile for different metal exchanged K-10 catalysts. Conditions: temperature = 111 °C, aniline to PhAc mole ratio = 2, catalyst weight = 0.25 g, total reactants weight = 5 g.
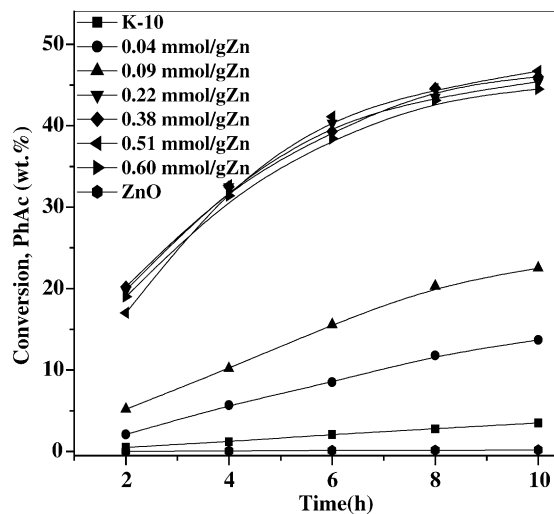

Fig. 4. Influence of zinc ion concentration on the activity of K-10 supported catalysts and activity of ZnO. Conditions: temperature = 111 °C, aniline to PhAc mole ratio = 2, catalyst weight = 0.25 g, total reactants weight = 5 g.

of ZnO in hydroamination reaction could be because of its lower Lewis acidity.

The strength of Lewis acidity of metal ions plays an important role in hydroamination reactions [16]. If the metal cation is a very weak Lewis acid, the formation of catalyst–substrate complex is either hindered or may not form at all. In contrast, if the metal cation is a strong Lewis acid, catalyst–substrate complex possibly too stable to undergo subsequent reactions. In other words, the intermediate Lewis acidity of the metal center facilitates the activation of the alkyne group in the presence of amine followed by coordination of the alkyne to the metal center and subsequent nucleophilic attack by the amine becomes possible. The Zn^{2+} ion is known as "moderate Lewis acid" cation owing to its moderate hardness, which explains the reason for higher activities shown by Zn/K-10 and Zn/H-beta catalysts in hydroamination of PhAc by aniline. Lewis acids like Al^{3+} present in K-10 as well as H-beta and other metal ions present in a little amount such as Na^+, K^+ and Ca^{2+}, Mg^{2+} in K-10 are responsible for smaller but noticeable activity shown by K-10 and H-beta. But lower activity shown by these metal ions may be due to their hardness property. Brönsted acidity decreases with increase in zinc ion concentration on K-10 (Fig. 1). Müller and co-workers studied in detail the role of Brönsted acidity in hydroamination reactions and the co-catalysis between Brönsted and Lewis acidity [21]. Brönsted acidity though does not seem to have profound effect in Zn/K-10 catalyzed hydroamination reaction, it appears that protons are involved in step III and step IV of the reaction (Scheme 2). It may facilitate 1,3-proton shift in 2-ammonioalkenyl zinc complex through protonation of the carbon attached to the metal and in turn helps in the cleavage of metal–carbon bond (step III). Brönsted acidity can also facilitate the formation of final product imine by the rearrangement of intermediate enamine in the last step. Moreover, reversible protonation of amines can enhance the possibility of the selective interaction of acetylenic bond with the metal center in the step I of the reaction. Hence, Brönsted acidity could help in enhancing the catalytic activity, when present in the vicinity of Lewis acidic zinc centers.

3.4. Optimization of reaction conditions

Zn/K-10 with 0.22 mmol/g zinc concentration was used to optimize the reaction conditions of intermolecular hydroamination of PhAC by aniline.

3.4.1. Effect of temperature

The reaction was studied by varying the temperatures (90–150 °C), keeping constant catalyst 0.25 g (5% of the total reactants weight) and aniline to PhAC mole ratio of 2. Conversion of PhAc as a function of temperature is shown in Fig. 5. Following the initial rate approach, the graph of ln rate versus $1/T$ was plotted, which gave a straight line and the activation energy calculated from the slope was found to be 50.4 kJ/mol. The Markovnicov addition product phenyl-(1-phenylethylidene) amine formed with 100% selectivity.
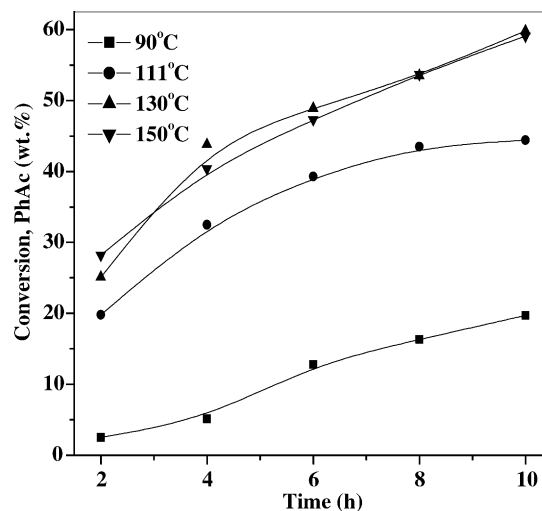

Fig. 5. Effect of temperature. Conditions: catalyst = 0.22 mmol Zn/K-10, aniline to PhAc mole ratio = 2, catalyst weight = 0.25 g, total reactants weight = 5 g.

Though the reflux temperature in this reaction is 111 °C (b.p. of toluene), the conversion of PhAc increased sharply when temperature was increased to 130 °C. There was not much change in conversion with further increase in temperature. The conversion decreased below reflux temperature (90 °C). Hence 130 °C was found to be suitable for the reaction and used for further optimization.

3.4.2. Effect of mole ratio

The reaction was carried out with aniline to PhAc molar ratios ranging between 2 and 15 keeping constant catalyst (0.25 g) and 130 °C. The results are shown in Fig. 6. Data collected over 10 h shows that change in aniline to PhAc mole ratio (from 2 to 5) has little influence on the conversion
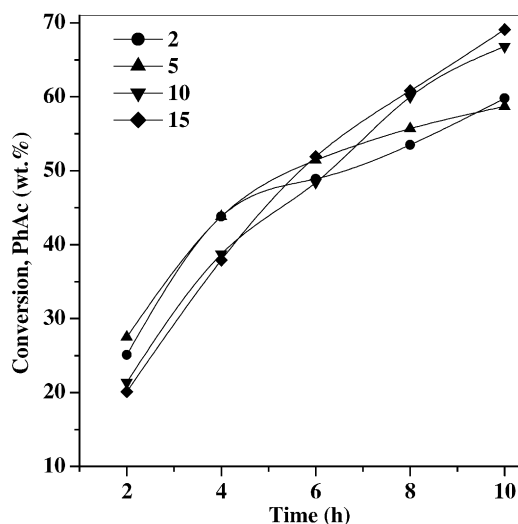

Fig. 6. Effect of aniline to PhAc mole ratio. Conditions: catalyst = 0.22 mmol Zn/K-10, temperature = 130 °C, catalyst weight = 0.25 g, total reactants weight = 5 g.
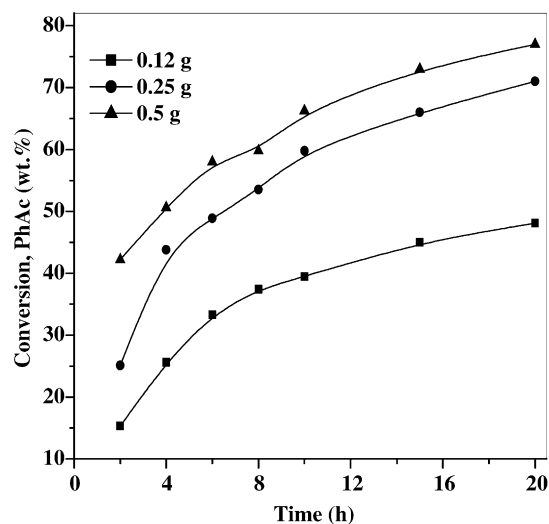
Fig. 7. Effect of catalyst concentration and reaction time. Conditions: catalyst = 0.22 mmol Zn/K-10, temperature = 130 °C, aniline to PhAc mole ratio = 2, total reactants weight = 5 g.

of PhAc. However, the conversion increased by 8% as the mole ratio increased from 5 to 10 and there was no change in conversion thereafter. After 6 h, conversion of PhAc was the same for all mole ratios studied. Hence, higher concentration of aniline in the reaction must be hindering the rate of hydroamination preventing the π coordination of PhAC with the metal center (Scheme 2).

3.4.3. Effect of catalyst concentration and reaction time

To study the effect of catalyst concentration, the reaction was carried out at 130 °C with aniline to PhAc mole ratio 2 by varying catalyst weight (0.12–0.5 g) and the results are shown in Fig. 7. The conversion of PhAc increased with increase in catalyst concentration as expected. There was linear increase in conversion up to 6 h and later there was marginal increase in the range of 6–20 h. At the end of 20 h, maximum conversion of PhAc (77%) was obtained for 0.5 g of catalyst with 100% selectivity for phenyl-(1-phenylethylidene) amine. Catalyst recycling was performed thrice by following the standard procedure and the conversion was the same as that of the fresh catalyst in all the cycles.

4. Conclusions

Intermolecular hydroamination of phenyl acetylene (PhAc) by aniline to give phenyl-(1-phenylethylidene) amine

was studied in detail using Zn^{2+} exchanged K-10 catalysts. The reaction was highly regioselective and only the Markovnicov addition product was formed. The activity of Zn/H-beta and Zn/K-10 were nearly the same at the end of 10 h and others followed in the order Zn/silica, H-beta, clay and silica. Zn^{2+} exchanged K-10 showed the highest activity compared to other metals. It is also found that Lewis acidic zinc sites along with Brönsted acid sites of the catalyst play an important role in enhancing the catalytic activity. Zn/K-10 is cost effective and active catalyst for intermolecular hydroamination of alkynes.

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