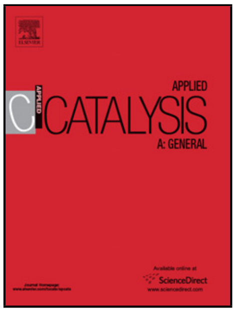


Title: Encapsulation of copper(I)-Schiff base complex in NaY nanoporosity: An efficient and reusable catalyst in the synthesis of propargylamines via A^3-coupling (aldehyde-amine-alkyne) reactions

Author: <ce:author id="aut0005"> Hossein Naeimi<ce:author id="aut0010"> Mohsen Moradian

PII: S0926-860X(13)00128-2
DOI: http://dx.doi.org/doi:10.1016/j.apcata.2013.03.008
Reference: APCATA 14129

To appear in: *Applied Catalysis A: General*

Received date: 13-11-2012
Revised date: 13-2-2013
Accepted date: 6-3-2013

Please cite this article as: H. Naeimi, M. Moradian, Encapsulation of copper(I)-Schiff base complex in NaY nanoporosity: An efficient and reusable catalyst in the synthesis of propargylamines via A^3-coupling (aldehyde-amine-alkyne) reactions, *Applied Catalysis A, General* (2013), http://dx.doi.org/10.1016/j.apcata.2013.03.008

Encapsulation of copper(I)-Schiff base complex in NaY nanoporosity: An efficient and reusable catalyst in the synthesis of propargylamines via A^3-coupling (aldehyde-amine-alkyne) reactions

Hossein Naeimi* Mohsen Moradian
Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, 87317, I.R.Iran
Fax No: +98-361-5912397
E-mail address: naeimi@kashanu.ac.ir

Highlights

Development of New N_2S_2-donor *salen*-type ligand.

Preparation of New host/NaY–guest/Cu(I) N_2S_2-thiosalen complex material.

High activity of the hybrid material in the synthesis of propargylamines.

High stability and catalytic activity of the catalyst due to the rich electron-donating.

Reusability of the catalyst with negligible leaching of metal ion in the A^3-coupling reaction.

Abstract

Nanodimensional microreactor containing bis[2-(phenylthio)benzylidene]-1,2-ethylenediamine copper(I) complexes, $[Cu(N_2S_2)]X$-Y (X=CN, Cl, Br, I) have been successfully prepared. This nano composite used as a catalyst in one-pot multicomponent coupling reaction of aldehydes, amines and alkynes toward synthesis of propargylamines. The copper (I) complex with N_2S_2 donor Schiff base ligand was readily trapped in the nanocavity of zeolite-Y through a template synthesis method (TS). However two consecutive process in the liquid phase were performed: (i) preparing a solution of $[Cu(MeCN)_4]X$ and coordinated with 2-(phenylthio)-benzaldehyde in the presence of zeolite-Y. This process caused the inclusion of $[Cu(MeCN)_2(S_2O_2)]X$ complex into the nanopores of Y via pre-adsorption method. (ii) Template synthesis of the $[Cu(MeCN)_2(N_2S_2)]X$-Y, through Schiff condensation between $[Cu(MeCN)_2(S_2O_2)]X$ and 1,2-ethylenediamine moiety into the nanopores of NaY. The resulting catalysts were fully characterized by spectroscopic techniques such as AAS, FT-IR, BET isotherm, XRD, UV-Vis and TGA. The results was indicated the encapsulation of Y-zeolite with copper(I) complex of N_2S_2 donor ligand. The catalytic activity of this nanocomposite material was investigated for preparation of propargylamines via three-component reaction of aldehydes, amines and alkynes. Also, the effective factors on this condensation reaction such as; reaction temperature, solvent, catalyst loading, leaching and reusability of the catalyst were discussed.

Keywords:
N_2S_2-Schiff base, Cu(I)-complex, heterogeneous, Y-zeolite, catalyst, propargylamine

1. Introduction

The C-C bond formation reactions such as preparation of propargylamines catalyzed by transition-metal complexes are among the most important fundamental transformations in synthetic chemistry [1]. The propargylamines are significant intermediates for synthesis of various nitrogen compounds as pharmaceutical active ingredients [2] and natural products such as β-lactams, peptides, isosteres and therapeutic drug molecules [2, 3]. These compounds can be obtained by an A^3-coupling reaction between aldimines and activated C-H of alkynes[4] via copper source as heterogeneous catalyst [5-10]. However, copper (I) halides[11] such as; CuCl[12], CuBr[13], and CuI[6] or coordinated with organic donor ligands have been used as catalysts[14, 15].

Schiff base ligands are easily synthesized and coordinate with almost all metal ions to form relative complexes. These complexes can catalyze various reactions depending on the type of metal ion [16, 17]. However, some of the homogeneous transition metal complexes demonstrate noteworthy catalytic properties (activities and selectivity). The homogeneous catalysts are unsuitable for separating from the reaction medium and making their reuse difficult and infecting the reaction products. Heterogenization of homogeneous transition metal catalysts via immobilization on solid supports[18] can mitigate these problems. The host-guest zeolite structures suggest an ideal support for the immobilization of metal complexes [19, 20]. Zeolite encapsulated metal complexes (ZEMC) could provide an opportunity for easy recovering and recycling of the catalyst[21], facile product purification and possibly, continuous or multiple processing of compounds[10, 22, 23].

Recent reports in this field have included the development of recoverable and reusable catalysts through organic- inorganic hybrid materials. Li and Wang, have reported an efficient and reusable heterogeneous copper (I) organic-inorganic hybrid material (SiO_2-CHDA-Cu^I) as a catalyst in this reaction[24]. Likhar et al., described an imine-functionalized copper complex immobilized on silica (SiO_2-Py-CuI) in acetonitrile at 90 ^oC[25], also Lei Wang and co-workers, prepared an N-heterocyclic carben (NHC) silica supported complex with CuI for the synthesis of propargylamines[26]. Immobilizing the copper metal as an efficient catalyst in the reaction via silica supports[27], molecular sieves[28], magnetite[29], zeolites[30], Pybox complexes on polystyrene resin[31] and Cu(I)–MOF[32] as heterogeneous catalysts were as well reported.

We developed a new N_2S_2-donor ligand of phenylthioether used as phenolic units of Schiff base (N_2O_2 salen-type), and coordinated with copper(I) halides within nanopores of Y-zeolite. Due to the electron-donating rich character of sulfur atoms, the thiosalen ligand increase the stability of the complex and improve catalytic activity of copper(I) especially in the A^3-coupling reaction of aldimines and alkynes toward propargylamines. The reaction does not require any co-catalyst and after completion of the reaction, the catalyst was recovered by filtration and reused several times with only a slight decrease of activity under the same reaction conditions.

2. Experimental

2.1. Material and physical measurements

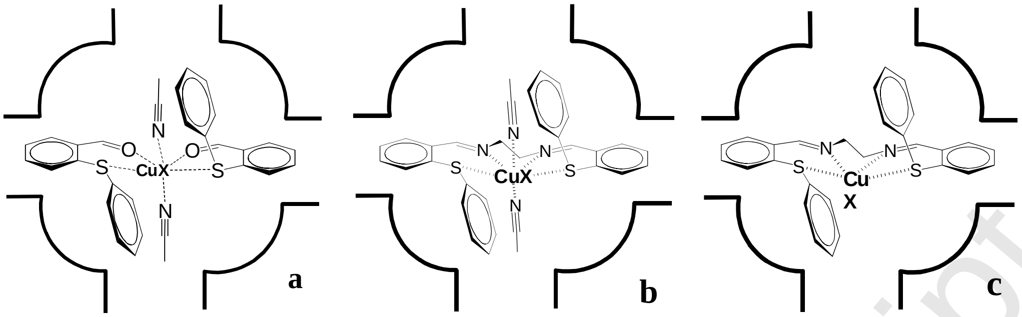
All the solvents were purchased from Merck Company (reagent grades) and were used as received unless otherwise specified. The NaY zeolite with the Si:Al ratio of 2.53 in powder form was purchased from Aldrich (Art No. 334448); IR spectra were recorded as KBr pellets on a Nicolet FT-IR spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. XRD patterns were recorded by an X'PertPro (Philips) instrument with 1.54 Ångström wavelengths of x-ray beam and Cu anode material. Nitrogen adsorption measurements were performed at 77K using a Coulter Ofeisorb 100CX instrument. Micropore volumes were determined by the *t*-method. The copper determination was carried out by a Unicam 929 model flame A. A. spectrophotometer.

2.2. Synthesis of 2-phenylthiobenzaldehyde

Freshly prepared magnesium methoxide (0.90 g, 10 mmol) was placed in a 50-mL reaction flask. N,N-Dimethylformamide (30 ml), 2-nitrobenzaldehyde (1.50 g, 10 mmol), and thiophenol (1.10 g, 10 mmol) were added and stirred at 80 ºC for 4 hours. The progress of the reaction was monitored by TLC, after completion of the reaction, water (50 ml) was added, and the aqueous solution was extracted twice with ethyl acetate (2×10 ml). The combined organic layers were dried over magnesium sulfate. The solvent was evaporated at a reduced pressure to produce the yellow oil, followed the purification by column chromatography using *n*-hexane/ethyl acetate (8/2) as eluent to afford 2-phenylthiobenzaldehyde (1.85 g 87% yield). IR (thin film): 3060 (H-Ar), 2846, 2738 (HCO), 1686 (C=O), 1584, 1445 (C=C, Ar), 1392, 1299, 1195, 751, 694. ^{1}H NMR ($CDCl_3$): 10.38 (*s*, 1 H, HC=O), 7.88 (*s*, 1 H, Ar), 7.26-7.43 (*m*, 7 H, Ar), 7.10 (*s*, 1 H, Ar). ^{13}C NMR ($CDCl_3$): 126.3, 128.4, 129.7, 130.3, 131.9, 133.1, 133.2, 133.7, 134.1, 141.5, 191.4. MS: 215 ($[M+1]^+$, 1.5), 215 (M^+, 12), 185 (45), 109 (74), 105 (23), 76 (100). Anal. Calcd. for $C_{13}H_{10}OS$ (214.28): C 72.8, H 4.7; Found: C 72.7, H 4.6[33].

2.3. Preparation of the catalyst $[Cu(N_2S_2)]X@Y$ (X=Cl, Br, I, CN)

Two consecutive process was done toward preparation of guest $[Cu(N_2S_2)]X$ /host (Y-zeolite) nanocomposite material. First of all, 1.0 mmol of each one of the CuCl, CuBr, CuI and CuCN as halides of copper(I), was added to 25 ml acetonitrile at 50 °C with continues stirring for about 2 h to give relative clear solutions of $[Cu(MeCN)_4]X$ (X=Cl, Br, I, CN) complexes. These four solutions were used during the preparation of target catalyst in the subsequent processes. To each one of these solutions, Zeolite-Y 2 g (previously dried in a vacuum oven in 80 °C for 10 h) was added, and the mixture was stirred for 5 h at room temperature. A solution of 2-phenylthiobenzaldehyde (2.0 mmol, 0.430 g) in 10 ml methanol was added and with further stirring at 50 °C for 15 h, the $[Cu(MeCN)_2(S_2O_2)]X@Y$ complexes (**a**) was prepared. The reaction mixture was filtered off and the solid collected and placed immediately in a new reaction container. A solution of 1,2-ethylenediamine (10 mmol, 0.6 g) in 10 ml absolute ethanol was added to the modified zeolite. The suspensions were stirred for 20 h under reflux conditions. The solid was collected, washed with ethanol (3×10 ml) and then $CHCl_3$ (3×10 ml) till the filtrate was free from any organic moieties (by TLC of filtrate) content. The modified zeolite (**b**), was dried at 60°C under vacuum overnight to obtain the corresponding nanoscale microreactors host (Y zeolite) /guest $[Cu(N_2S_2)]X$ (X= Cl, Br, I, CN) materials as light orange powders (**c**). Before characterization, the obtained catalysts were soxhlet extracted for 3 h in methanol to remove the remaining uncomplexed metal and species adsorbed on the external surface of the zeolite.



2.4. General procedure for the synthesis of propargylamines by the catalyst

All of the reactions were carried out at 70 ^{o}C in a 25 ml flask equipped with a magnetic stirring bar and reflux condenser. In a typical procedure, to a mixture of the selected aldehyde (1.0 mmol), the selected secondary amine (1.1 mmol) and the selected alkyne (1.2 mmol) in dichloroethane (DCE) as solvent, 697 mg from desired catalyst (containing 3 mol % copper based on copper halide) was added. The final mixture was stirred at 70 ^{o}C, after completion of the reaction (monitored by TLC); the resulting mixture was then filtered through a pad of celite and solid catalyst washed with CH_2Cl_2 (3×5 ml) and methanol (3×5 ml). The filtered was evaporated under reduced pressure to give a crude product as viscous oil. The product was purified over silicagel by column chromatography (10% EtOAc in hexane as eluent) to give the desired propargylamine.

3. Results and discussion

Zeolite-Y is an inert microporous crystalline aluminosilicate that forming nano-cavities and nano-channels of strictly regular dimensions. The NaY consists of almost spherical 1.3 nm cavities interconnected through apertures of 0.74 nm diameters[34]. The structure of the large size of the encapsulated homogeneous catalysts and their rigidity make them difficult to escape out of the zeolite cages. Since, the catalyst is usually comprised of several specific active sites, the atomically uniform dispersion of metal catalysts is highly beneficial for significant improvement of catalytic action[35].

3.1. Characterization of the catalyst

The Y-zeolite encapsulated with N_2S_2 thiosalen copper(I) complex were investigated by infrared, UV-Vis, XRD pattern, thermal gravimetry, BET theory and atomic absorption spectroscopy.

FT-IR spectroscopy is very important technique and can provide valuable information of the crystalinity and on the encapsulated metal complex inside the host zeolite. A comparison between the IR spectra of catalyst with that of the initial NaY indicates the presence of the organometallic complex inside the zeolite cavities (Fig. 1). The FT-IR spectra of NaY is dominated by some of the major zeolite framework bands in the range of 720-790 cm^{-1} ν_s (Si-O), 1020 cm^{-1} (Si-OH), 1130 cm^{-1} ν_{as} (Si-O and Al-O) and 3550 cm^{-1} for isolated silanol (Si-OH)[36, 37]. These bands detected in all of the encapsulated zeolite and support the fact that the encapsulation process does not modify the zeolite structure.

The IR spectra of the free ligand showed the strong band at 1614 cm^{-1} is assigned to stretching vibration of C=N group. This band shift to lower position by 6-9 cm^{-1} in complexes that suggests coordination of copper through C=N functional groups (Fig. 1). The encapsulated complexes exhibit very similar IR data concerning those of the corresponding free complexes and confirm the presence of $[Cu(N_2S_2)]X$ in the nanoporosity of Y-zeolite, and suggest that its structure is almost identical to that of the free. The intensity of IR bands of $[Cu(N_2S_2)]Cl@Y$ depends on their loading and normally is weaker that, due to the low concentration of the complexes. For instance, in the Fig. 1, we show the FT-IR spectra for $[Cu(N_2S_2)]Cl$ complex (a), NaY (b), and $[Cu(N_2S_2)]Cl@Y$-zeolite (c).

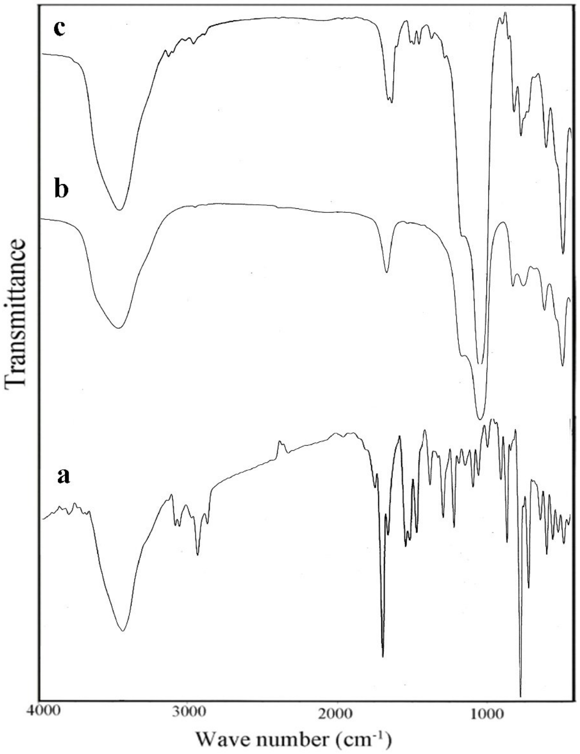


Fig. 1. FT-IR spectra of $[Cu(N_2S_2)]Cl$ complex (a), NaY (b) and $[Cu(N_2S_2)]Cl@Y$-zeolite (c)

Powder X-ray diffraction patterns of zeolite-Y are normally measured in the range 10–70°. The X-ray diffraction (XRD) patterns of modified NaY with organo-copper complex are similar to those of untouched zeolite (Fig. 2). Upon encapsulation, a very slight change in the intensity and broadening of the peaks was observed which can be shown a negligible loss that may occur in crystallinity of the Y-zeolite [38, 39]. This pattern also confirms that the framework of the NaY does not destroy, and the complexes were well distributed in the pores. We present the XRD pattern of Y-zeolite (a) and [Cu(N_2S_2)]Cl@Y nanocomposite (b) in the Fig. 2.

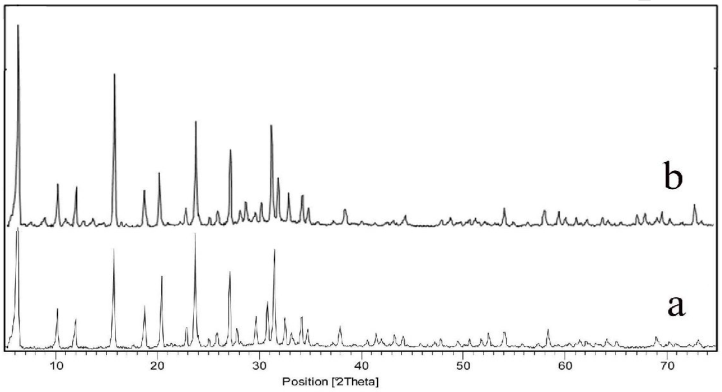


Fig. 2. X-ray diffraction patterns of (a) zeolite-Y and (b) zeolite encapsulated CuCl-thiosalen

The electronic spectrum of thiosalen ligand shows two bands at 248 and 372 nm in CH_2Cl_2 as solvent which arise due to π→π* and n→π* transitions. Since no d→d transitions are expected for d^{10} complexes, the UV-vis bands of the [Cu(N_2S_2)]Cl complex at 454 nm are assigned to the metal-ligand charge transfer (MLCT) or ligand centered π→π* transitions [40]. The comparison of UV-Vis spectrums for ligand, complex and encapsulated nanoreactor (diffuse reflective spectrum) in Fig. 3 confirmed the incorporation of thiosalen-CuCl complex into the Y-zeolite supercages.

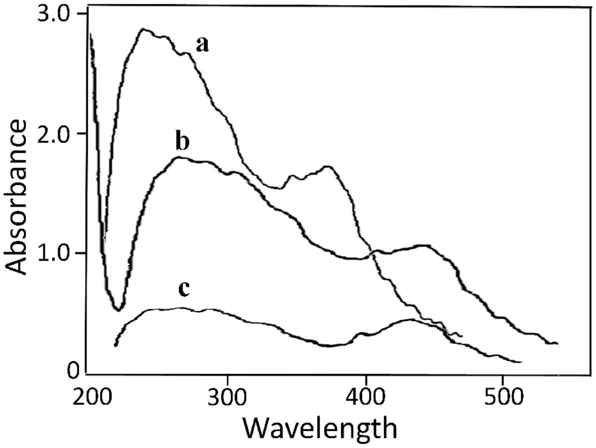


Fig. 3. Uv-vis and DRS absorption of neat thiosalen

ligand (a), $[Cu(N_2S_2)]Cl$ complex (b) and $[Cu(N_2S_2)]Cl@Y$ (c)

Data on BET surface area and pore volume of the zeolite and modified zeolite are presented in Table 1. An effective decrease in BET surface area was observed on modified Y-zeolite with the reduction in the pore volume.

Table 1
Pore volume and surface area of the encapsulated zeolite getting from nitrogen adsorption isotherm

Sample	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]
NaY	545	0.32
$[Cu(N_2S_2)]Cl$-NaY	384	0.21
$[Cu(N_2S_2)]Br$-NaY	379	0.19
$[Cu(N_2S_2)]I$-NaY	364	0.20
$[Cu(N_2S_2)]CN$-NaY	373	0.22

[a] Monolayer equivalent area calculated as explained in reference[41]
[b] Calculated by *t*-method

Since zeolite framework structure is not affected by encapsulation (as shown by XRD pattern) these reductions in the surface area and pores volume, provides direct evidence for the presence of complexes in the cavities[42]. Fig. 4 shows the adsorption/desorption N_2 isotherms (77 K) for the parent zeolite and $[Cu(N_2S_2)]Cl$-NaY encapsulated complex. The BET isotherm of the encapsulated complex is characterized by a slightly sloped or plateau form, and also by a low degree of hysteresis. This is in agreement with the XRD analysis, which indicated no significant changes in the crystallinity patterns of the zeolite structures.

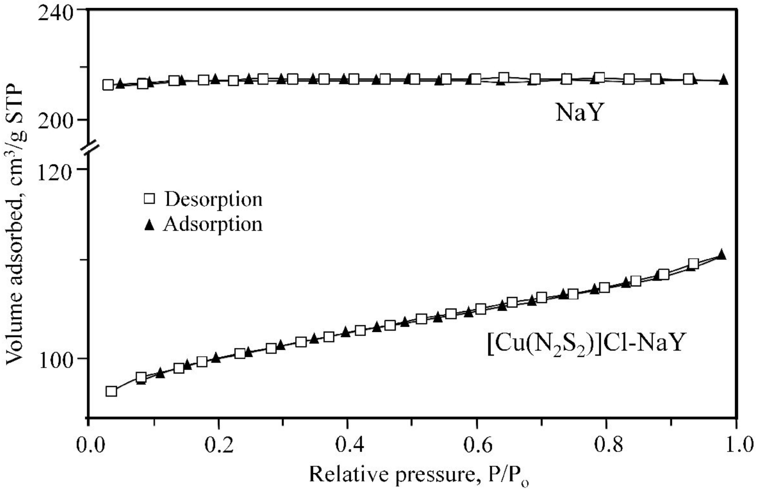


Fig. 4. The nitrogen adsorption/desorption isotherms for the NaY and encapsulated complex

The thermal stability of catalyst was studied by TGA and DTA. Y-zeolite shows an endothermic two stage of weight loss in the 50-230 °C due to the (i) physically adsorbed water on surface and (ii) chemisorbed intra zeolite water in the form of OH groups. The thermal gravimetric curves of NaY and $[Cu(N_2S_2)]Cl@NaY$ are shown in Fig. 5. The mass loss in the temperature range between 30-160 °C is related to the expulsion of adsorbed water. The mass loss in the temperature range between 290-580 °C can be due to the removal of Schiff base ligand. The copper halide was ultimately oxidized into CuO and the final residue of decomposition was found to be zeolite and CuO. However, these results confirm that the CuCl-thiosalen complex entrapped to the nanocavity of zeolite pores.

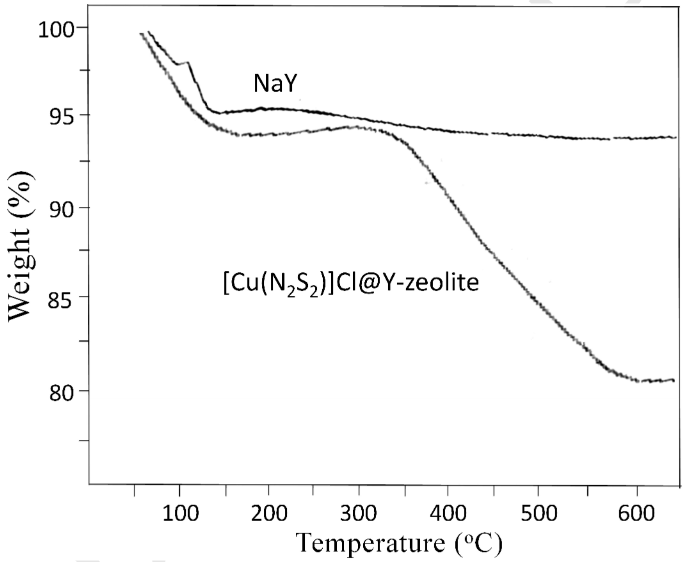


Fig. 5. TGA pattern of NaY and $[Cu(N_2S_2)]Cl@Y$-zeolite

Analysis of the copper ions in the zeolite samples was carried out by the destroying of zeolite lattice using atomic absorption technique. A known weight of the sample was treated with concentrated hydrochloric acid followed by concentrated nitric acid. The solution was maintained at boiling temperature for 3 hours on an oil bath. It was then cooled, diluted with water and filtered using ash-less filter paper and was used for the estimation of copper. Consequently, the amounts of copper were obtained about 0.041–0.045 mmol/g of encapsulated zeolite (Table **2**).

Table 2

Amounts of the copper (I) loaded in the nanoporosity of Y

Entry	catalyst	Cu (mmol/g^a)
1	$[Cu(N_2S_2)]Cl$-NaY	0.043

2	$[Cu(N_2S_2)]Br\text{-}NaY$	0.041
3	$[Cu(N_2S_2)]I\text{-}NaY$	0.041
4	$[Cu(N_2S_2)]CN\text{-}NaY$	0.045

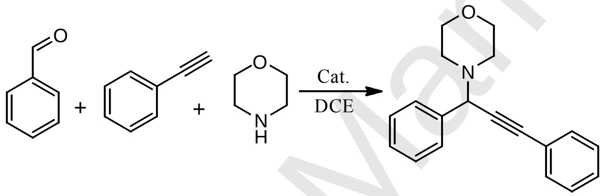
[a] Determined by atomic absorption spectroscopy

3.2. Activity of the catalyst

The catalytic Mannich reaction of benzaldehyde, morpholine and phenylacetylene was performed in the presence of $[Cu(N_2S_2)]X@Y$ as a heterogeneous and reusable catalyst (Table 3, entries 4-7). As it can be seen in Table 3, all of the encapsulated Cu(I) solid catalysts shown good results for this reaction. However, comparing activities of four species of the prepared catalyst's evidence that, the chloride as copper halide gave a higher conversion and was found to be the most effective one (Table 3, entry 4).

Table 3

Search for optimal reaction conditions[a]



Entry	Catalyst (mol %)	Temp. (°C)	Time (h)	Yield (%)[b]
1	-	70	20	-
2	NaY	70	20	-
3	$[Cu(N_2S_2)]Cl$	70	17	60
4	$[Cu(N_2S_2)]Cl\text{-}Y$ (3 mol %)	70	12	90
5	$[Cu(N_2S_2)]I\text{-}Y$ (3 mol %)	70	12	84
6	$[Cu(N_2S_2)]Br\text{-}Y$ (3 mol %)	70	12	73
7	$[Cu(N_2S_2)]CN\text{-}Y$ (3 mol %)	70	12	65
8	$[Cu(N_2S_2)]Cl\text{-}Y$ (3 mol %)	60	15	82
9	$[Cu(N_2S_2)]Cl\text{-}Y$ (3 mol %)	50	20	74
10	$[Cu(N_2S_2)]Cl\text{-}Y$ (3 mol %)	30	90	67
11	$[Cu(N_2S_2)]Cl\text{-}Y$ (1 mol %)	70	20	19
12	$[Cu(N_2S_2)]Cl\text{-}Y$ (5 mol %)	70	10	90
13	$[Cu(N_2S_2)]Cl\text{-}Y$ (10 mol %)	70	10	90

[a] Benzaldehyde (1.00 mmol), Phenylacetylene (1.20 mmol), morpholine (1.10 mmol), encapsulated Cu(I) catalyst and DCE (5 ml) as solvent.

[b] Isolated yields based on benzaldehyde.

The occurring of reaction in the presence of NaY under the same reaction conditions was shown any product even after the prolong reaction time. This was resulted that the host zeolite was inert in this reaction (Table 3, entries 1, 2). Also, by using of the $[Cu(N_2S_2)]Cl$ as catalyst in the reaction was obtained the product in low yield. While, the used encapsulated complexes in this reaction was shown the higher activity than ones because of the site isolation of the copper ion (Table 3, compare entries 3 and 4).

When 3 mol % copper(I) as a heterogeneous catalyst loaded in the reaction mixture, the reaction was generally completed (Table 3, entry 4). With attention to the results that show in this Table, the time was inversely proportional to the temperature. We also loaded different amounts of the selected catalyst in this reaction (Table 3, entries 11-13) in order to optimization. Thus, the optimized reaction conditions for catalyst loading and temperatures of the reactions are 3 mol % of catalyst based on copper and 70 °C respectively.

The solvents also play an important role in this three-component coupling Mannich type reaction. In an effort to seek improved yields and a more effective solvent, various solvents were screened in the reaction of benzaldehyde, morpholine and phenylacetylene under similar reaction conditions (Table 4). With attention to the results in Table 5, DCE provided excellent yields and proved to be the solvent of choice. Polar solvents such as DMSO, DMF and acetonitrile were found to be suited for this reaction with comparable yields (Table 4, entries 7-9). Due to the leaching of copper ion from the solid catalyst in these solvents (20-24 %), make these solvents unfavorable for this reaction. The optimum mol ratio of aldehyde, amine and alkyne was found to be 1:1.1:1.2 respectively.

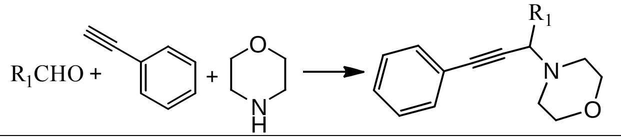
Table 4
Solvent study in the A^3-coupling reaction toward propargylamine synthesis[a]

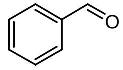
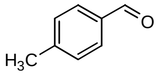
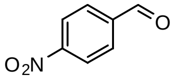
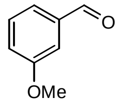
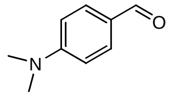
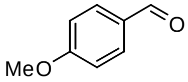
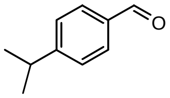
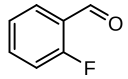
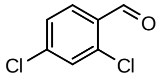
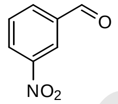
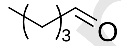
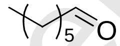
Entry	solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	DCE	70	12	90
2	$PhCH_3$	70	12	81
3	CH_2Cl_2	40	25	47
4	$CHCl_3$	60	25	55
5	Cyc. Hex.	70	12	5
6	MeOH	65	20	38
7	DMSO	70	12	79
8	MeCN	70	12	83
9	DMF	70	12	80

[a] Benzaldehyde (1.00 mmol), Phenylacetylene (1.20 mmol), morpholine (1.1 mmol), 697 mg. heterogeneous $[Cu(N_2S_2)]Cl$-Y as catalyst that equal with 0.03 mmol copper.
[b] Isolated yields.

In order to investigate the scope and generality of the encapsulated zeolite as solid catalyst in the A^3-coupling reaction, several aldehydes with variety of functional groups were applied. The obtained results are summarized in Table 5**.** Electron-poor aryl aldehydes afforded high yields (Table 5**,** entries 3, 8-10) in compare with an electron donating group in entries 4-6.

Table 5
Zeolite-Y encapsulated Cu(I) catalyzed three-component synthesis of substituted propargylamines[a]



Entry	aldehyde	Product	Time (h)	Yield (%)[b]	Ref.
1		**a**	12	90	[10, 30]
2		**b**	14	87	[24, 43]
3		**c**	12	91	[30]
4		**d**	14	85	[22]
5		**e**	17	78	[22]
6		**f**	19	87	[24, 30, 43]
7		**g**	15	84	[43]
8		**h**	13	83	[30]
9		**i**	20	86	[24]
10		**j**	17	87	[43]
11		**k**	16	82	[30]
12		**l**	16	80	[24]

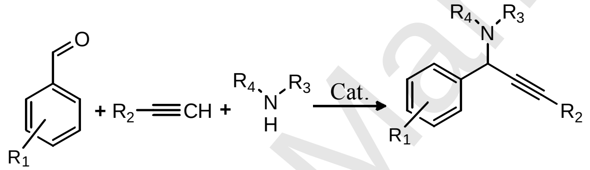
[a] Aldehyde (1.0 mmol), Phenylacetylene (1.20 mmol), morpholine (1.1 mmol), heterogeneous Cu(I) catalyst (680 mg, contains 0.03 mmol of CuCl) in DCE (5.0 ml) at 70 °C.

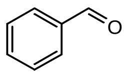
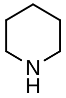
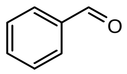
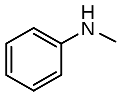
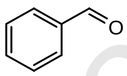
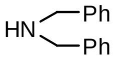
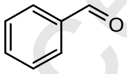
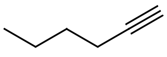
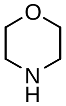
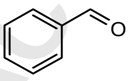
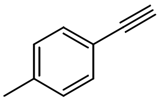
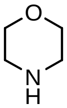
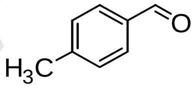
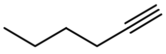
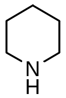
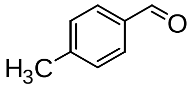
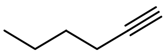
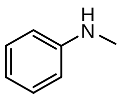
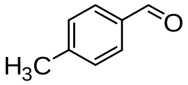
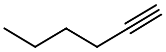
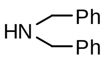
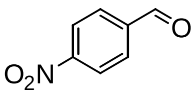
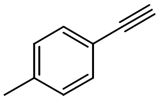
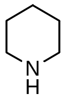
[b] Isolated yields based on aldehyde

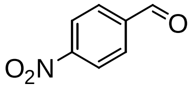
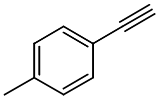
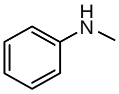
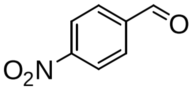
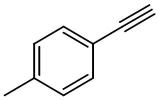
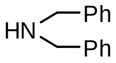
To examine the scope of this A^3-coupling reaction to alkyne and secondary amine substrates, various types of these moieties were tested in the presence of the solid catalyst in optimized conditions (Table 6). The coupling reaction proceeded readily and smoothly to afford the corresponding propargylamines in good to excellent yields. Among the various amines that studied, morpholine and piperidine as aliphatic amines gave higher yields than that aromatic phenylmethylamine. However, the dibenzylamine afforded a poor yield of the desired products Table 6, entries 3, 8, 11).

Aromatic alkynes and n-pentyne as aliphatic alkyne also underwent the corresponding coupling reaction smoothly and generated the products in excellent yields under the present reaction conditions.

Table 6
Formation of propargylamine compounds through three-component coupling reaction[a]



Entry	Aldehyde	Alkyne	sec. amine	Product	Yield (%)[b]	Ref.
1		$\mathrm{Ph}{-}{\equiv}{-}\mathrm{CH}$		**m**	88	[3, 10, 24]
2		$\mathrm{Ph}{-}{\equiv}{-}\mathrm{CH}$		**n**	85	[22]
3		$\mathrm{Ph}{-}{\equiv}{-}\mathrm{CH}$		**o**	81	[10]
4				**p**	84	[30]
5				**q**	87	[43]
6				**r**	86	[10]
7				**s**	83	[30]
8				**t**	83	[10]
9				**u**	89	[3, 10]

10				**v**	84	[30]
11				**w**	82	[22]

[a] Aldehyde (1.0 mmol), alkyne (1.20 mmol), secondary amine (1.1 mmol), heterogeneous Cu(I) catalyst (680 mg, contains 0.03 mmol of CuBr) in DCE (5 ml) at 70 °C.

[b] Based on isolated yields.

Zeolites with low ratios of Si/Al have a high number of compensating cations, which will produce electrostatic fields in channels and cavities. Fields of this magnitude in the internal voids of the pores, stabilize positive species such as metal ions in organometallic complexes as van der Waals contacts as same as behavior of highly polar and non-nucleophilic solvents. These interactions can be stabilize the encapsulated catalyst in the pores and enhance their catalytic activity in the reaction.

For catalyst leaching study, after occurring of the reaction in first step, the solid catalyst was separated by filtration. The liquid phase was subjected as solvent to further reaction with the new three moieties of starting substrates without any catalyst and under the same reaction conditions. However, there was no further conversion of moieties to desired products when the catalyst was removed from the reaction system. The reaction in the presence of filtrate cannot perform, and a negligible product was occurred (<6%) after 30 h reaction time. This means that the active catalyst did not leach from the zeolite. As analyzed on the final reaction solution using atomic absorption spectroscopy, provided <1% leaching of the copper metal from the heterogenized catalyst. In accord with the X-ray diffraction patterns of $[Cu(N_2S_2)]Cl@Y$ before and after the using in reaction media, the crystalinity of catalyst was preserved. The recyclability of the catalyst also was studied. After the reaction, the solid modified zeolite was recovered by filtration of mixture under vacuum using sintered glass funnel and thoroughly washed with CH_2Cl_2 (5 ml) and Et_2O (5 ml) respectively. The solid catalyst was dried on an oven 60°C and used for next reaction without any reactivation. In this case a slow decrease in yields was observed (Fig. 4). However, the solid catalyst can be reused for at least eight consecutive runs without major loss of activity.

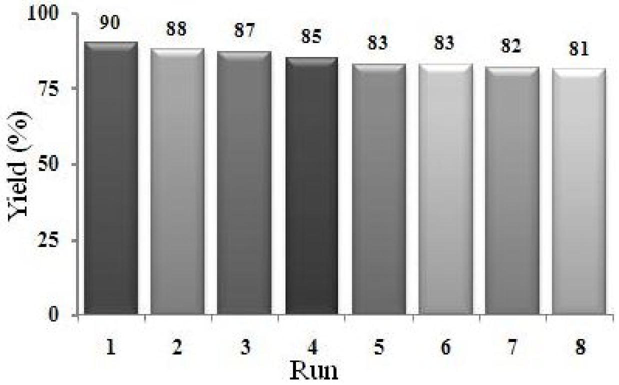


Fig. 4. Recyclability of the heterogeneous [Cu(N_2S_2)]Cl@Y as recoverable catalyst for the A^3-coupling reaction

4. Conclusion

The results show that the novel N_2S_2 donor ligand as organocopper (I) complex, [Cu(N_2S_2)Cl], can be encapsulated readily in the nano-dimentional cavities of zeolite-Y by template synthesis method (TS). This strategy appears to be remarkably efficient for the heterogenization of copper(I) catalysts based on Schiff base ligands. The immobilized organometallic complex show high activity in the synthesis of propargylamines via three-component coupling reaction. High conversions were obtained using the CuCl as copper halide, also over several cycles in dichloroethane as solvent the activity of catalyst was maintained. Furthermore, the catalyst could be readily recovered and reused, whilst no leaching was observed after utilization of the catalyst.

Acknowledgment

The authors are grateful to University of Kashan for supporting this work by Grant No. 159148/14.

References

[1] W. Shi, C. Liu, A. Lei, Chem. Soc. Rev. 40 (2011) 2761-2776.

[2] A. Kochman, J. Skolimowski, L. Gebicka, D. Metodiewa, Pol. J. Pharmacol. 55 (2003) 389-400.

[3] C. Wei, Z. Li, C.J. Li, Org. Lett. 5 (2003) 4473-4475.

[4] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879-2932.

[5] M.A. Youngman, S.L. Dax, J. Comb. Chem. 3 (2001) 469-472.

[6] T. Okamura, K. Asano, S. Matsubara, Synlett. 2010 (2010) 3053-3056.

[7] M.J. Albaladejo, F. Alonso, Y. Moglie, M. Yus, Eur. J. Org. Chem. 2012 (2012) 3093-3104.

[8] M. Kidwai, V. Bansal, K.M. N., A. Kumar, S. Mozumdar, Synlett. 2007 (2007) 1581-1584.

[9] I. Luz, F.X. Llabrés i Xamena, A. Corma, J. Catal. 285 (2012) 285-291.

[10] K.M. Reddy, N.S. Babu, I. Suryanarayana, P.S.S. Prasad, N. Lingaiah, Tetrahedron Lett. 47 (2006) 7563-7566.

[11] J.B. Bariwal, D.S. Ermolat'ev, E.V. Van der Eycken, Chem.-Eur. J. 16 (2010) 3281-3284.

[12] M.A. Youngman, S.L. Dax, J. Comb. Chem. 3 (2001) 469-472.

[13] J.B. Bariwal, D.S. Ermolat'ev, T.N. Glasnov, K. van Hecke, V.P. Mehta, L. van Meervelt, C.O. Kappe, E.V. Van der Eycken, Org. Lett. 12 (2010) 2774-2777.

[14] C.-J. Li, Acc. Chem. Res. 43 (2010) 581-590.

[15] W.J. Yoo, L. Zhao, C.J. Li, Aldrichimica Acta. 44 (2011) 43-50.

[16] I. Kuźniarska-Biernacka, O. Rodrigues, M.A. Carvalho, I.C. Neves, A.M. Fonseca, Appl. Organometal. Chem. 26 (2012) 44-49.

[17] F. Bedioui, Coord. Chem. Rev. 144 (1995) 39-68.

[18] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615-3640.

[19] R. Maggi, A. Bello, C. Oro, G. Sartori, L. Soldi, Tetrahedron. 64 (2008) 1435-1439.

[20] T. Boningari, A. Olmos, B.M. Reddy, J. Sommer, P. Pale, Eur. J. Org. Chem. 2010 (2010) 6338-6347.

[21] C.E. Song, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 101 (2005) 143-173.

[22] M.L. Kantam, S. Laha, J. Yadav, S. Bhargava, Tetrahedron Lett. 49 (2008) 3083-3086.

[23] P. Li, L. Wang, Y. Zhang, M. Wang, Tetrahedron Lett. 49 (2008) 6650-6654.

[24] P. Li, L. Wang, Tetrahedron. 63 (2007) 5455-5459.

[25] P.R. Likhar, S. Roy, M. Roy, M.S. Subhas, M.L. Kantam, R.L. De, Synlett. 18 (2007) 2301-2303.

[26] M. Wang, P. Li, L. Wang, Eur. J. Org. Chem. 2008 (2008) 2255-2261.

[27] B. Sreedhar, P.S. Reddy, C.S.V. Krishna, P.V. Babu, Tetrahedron Lett. 48 (2007) 7882-7886.

[28] A. Fodor, Á. Kiss, N. Debreczeni, Z. Hell, I. Gresits, Org. Biomol. Chem. 8 (2010) 4575-4581.

[29] M.J. Aliaga, D.J. Ramón, M. Yus, Org. Biomol. Chem. 8 (2010) 43-46.

[30] M.K. Patil, M. Keller, B.M. Reddy, P. Pale, J. Sommer, Eur. J. Org. Chem. 2008 (2008) 4440-4445.

[31] A. Weissberg, B. Halak, M. Portnoy, J. Org. Chem. 70 (2005) 4556-4559.

[32] J. Yang, P. Li, L. Wang, Catal. Commun. 27 (2012) 58-62.

[33] H. Naeimi, M. Moradian, Synlett. 23 (2012) 000A-000D.

[34] M. Salavati-Niasari, J. INCL. PHENOM. MACRO. 65 (2009) 349-360.

[35] M.R. Maurya, A. Kumar, J. Costa Pessoa, Coord. Chem. Rev. 255 (2011) 2315-2344.

[36] A.P.A. Marques, E.R. Dockal, F.C. Skrobot, I.L.V. Rosa, Inorg. Chem. Commun. 10 (2007) 255-261.

[37] P. McMorn, G.J. Hutchings, Chem. Soc. Rev. 33 (2004) 108-122.

[38] T. Joseph, D. Srinivas, C.S. Gopinath, S.B. Halligudi, Catal. Lett. 83 (2002) 209-214.

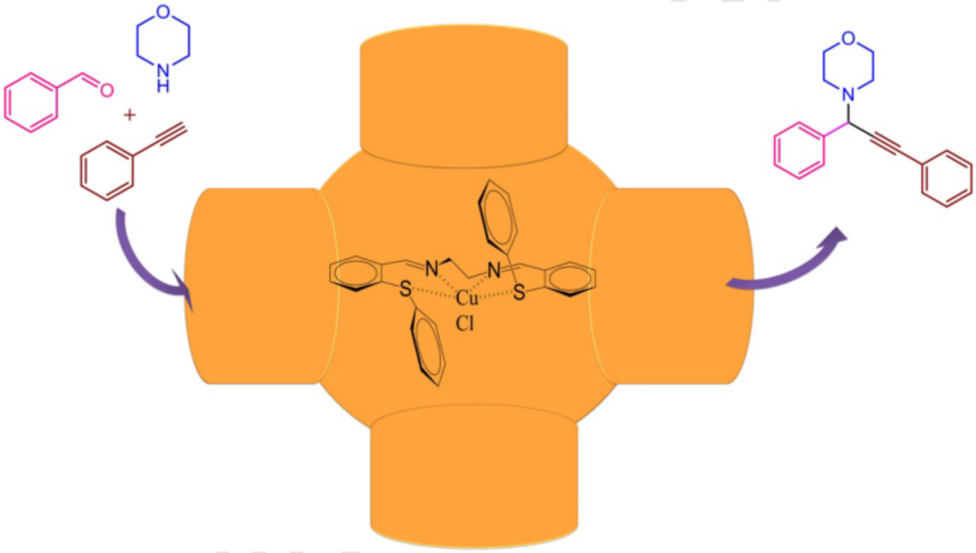
[39] A. Kozlov, K. Asakura, Y. Iwasawa, Microporous Mesoporous Mater. 21 (1998) 571-579.

[40] M. Morshedi, M. Amirnasr, A.M.Z. Slawin, J.D. Woollins, A.D. Khalaji, Polyhedron. 28 (2009) 167-171.

[41] K. Sing, D. Everett, R. Haul, L. Moscou, R. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603-619.

[42] K.J. Balkus, A.G. Gabrielov, J. INCL. PHENOM. MACRO. 21 (1995) 159-184.

[43] K. Namitharan, K. Pitchumani, Eur. J. Org. Chem. 2010 (2010) 411-415.


O
N
H
O
+
N
S
Cu
Cl
N
S
O
N