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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Cu@Furfural Imine-Decorated Halloysite as an Efficient Heterogeneous Catalyst for Promoting Ultrasonic-Assisted A³ and KA² Coupling Reactions: A Combination of Experimental and Computational Study

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Halloysite nanoclay (HNTs) was functionalized with (3-chloropropyl) trimethoxysilan and subsequently reacted with thiosemicarbazide and furfural to furnish furfural imine functionalized HNTs, which could serve as an efficient support for immobilization of copper species. The obtained catalyst, Cu@HNTs-T-F, was fully characterized using SEM/EDX, FTIR, ICP, TGA, XRD and BET. To present a theoretical description for experimental features of Cu@HNTs-T-F nano catalyst, we modeled and computationally assessed two coordination modes between copper acetate and HNTs-T-F ligand in the gas and solution phases. In this line, the mathematical properties of electron density functions were calculated and analyzed topologically *via* density functional theory (DFT) and quantum theory of atoms in molecules (QTAIM) approaches. Encouraged by our computational results, the catalytic activity of this new catalyst was studied for A³ and KA² coupling reactions of aldehydes or ketone, phenyl acetylene and amines under green, ultrasonic-assisted condition. The results established that the catalyst could promote the reaction to furnish the corresponding propargylamine derivatives in high yields in very short reaction times. Studying the reusability of the catalytic activity, indication the efficiency of the functionalized HNTs on anchoring the copper species. ICP-AES analysis established very low leaching of copper species upon reusing. This observation was attributed to the interactions of heteroatoms in functionalized HNTs with copper. Moreover, the results confirmed the heterogeneous nature of the catalysis.

Introduction

The importance of propargylamines arise from their utility as synthetic versatile intermediates for the synthesis of broad range of chemicals such as natural products, peptide isosteres, polyfunctional amino derivatives and different N-heterocycles such as β -lactams ¹⁻². To date various protocols and catalysts such as silver, zinc, nickel, cobalt, iron, gold and copper-based catalysts have been used for promoting terminal alkyne C-H bond activation and subsequently the reaction of activated alkyne with amines and aldehydes, referred as A³ coupling reaction, to furnish the corresponding propargylamines²⁻⁶. Although A³ coupling reaction is a superior method compared to traditional protocols for the synthesis of propargylamines, i.e. direct amination of propargyl halides, propargylic triflates, propargylic phosphates ²⁻⁴, or addition of alkynylmetal reagents to imines⁷, it is a log process that mostly need high temperature or inert atmosphere. Moreover, using transition or precious

metals render this process costly. Many studies have been focused on developing an efficient and green strategy due to the significance of this class of compounds $^{8-9}$.

Halloysite nanoclay (HNTs), with general formula of $(Al_2(OH)_4Si_2O_5.2H_2O)$ possess high surface area, tubular morphology and high mechanical strength. They belongs to the class of kaolinite group hydrated layered aluminosilicate ¹⁰⁻¹¹. In HNTs a monolayer of water separates the unite layers in HNTs. Moreover, the exterior and interior surfaces of HNTs are chemically different. Tetrahedral SiO₄ groups are located in the outer surface while the octahedral gibbsite Al(OH)₃ sheet forms the inner surface ¹².

Recently, functionalization of the surface of the HNTs is considered as a potent method for modification of the features of HNTs and expanding their applications. Notably, both surfaces of HNTs can be chemically modified. As an example Kepert et al. functionalized the surface of the HNTs by using γ aminopropyltriethoxysilane (APTES)¹³ and studied its characteristics. In another attempt, HNTs was aminefunctionalized by *N*- β -aminoethyl- γ -aminopropyl trimethoxysilane and then used for deposition of ultrafine noble

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DOI: 10.1039/C7NJ02272G Journal Name

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metallic nanoparticles such as Pd, Pt and Rh ¹⁴. In this line, Du et functionalized with APTES for catalytic purposes ¹⁵. Moreover, APTES functionalized HNTs was used for introduction of PVP-PdCl₂ and subsequent reduction for formation of Pd (0) nanoparticles for using in catalysis ¹⁶. More sophisticated functionalities such as poly(*N*-isopropylacrylamide) (PNIPAAM) was also covalently grafted on HNTs for supporting Pd nanoparticles ¹⁷. All these reports are indicative of the promising utility of functionalized HNTs for using as drug and enzyme carriers ¹⁹ and catalyst supports ²⁰⁻²¹. Additionally, HNTs proved their utilities for membrane for gas separation ²², photo degradation ²³, water treatment ²⁴⁻²⁵ and optical, magnetic and electrical applications ²⁰.

On the other hand, the improvement and extension in the application of HNTs such as their usage in the encapsulation of nonpolar chemicals for controlled release and nano-containers applications depends strongly on their surface chemical and physicochemical properties. However, the low activity of HNTs external surface results in weaker interfacial interactions and lowering the efficiency of HNTs for reinforcement and dispersion $^{26-29}$.

In continuation of our attempt to introduce heterogeneous and reusable catalysts $^{\rm 30-35}$ for promoting various organic reactions and developing green and environmentally benign protocols for efficient synthesis of chemicals ^{21, 35-40} and also armed with our previous computational modeling of structural, electronic and thermochemical properties of heterogeneous nanocatalysts ^{1-7, 39, 41-44}, herein, we present a novel heterogeneous catalyst based on functionalization of HNTs with (3-chloropropyl) trimethoxysilan, thiosemicarbazide and furfural and incorporation of copper species. The catalytic activity of the catalyst, Cu@HNTs-T-F, was studied for A^3 and KA^2 coupling reaction of aldehydes or ketone, phenyl acetylene and amines under ultrasonic irradiation in aqueous media (Scheme 1). Furthermore, the reusability of the catalyst for four reaction runs was studied. The nature of the catalysis was also determined by investigating the leaching of the copper species by using ICP-AES analysis. Considering the importance of understanding the surface chemical and physicochemical properties, we also concentrated on the computational modeling of HNTs surface and their functionalization modes to describe and predict immobilization behavior of copper on HNTs surface. Strictly speaking, we concentrated on the quantitative description of structural and electronic features of interactions between copper acetate (denoted as Cu(OAc)₂) and thiosemicarbazide functionalized HNTs modified with furfural (denoted as HNTs-T-F) via density functional theory (DFT) 45 and quantum theory of atoms in molecules (QTAIM)⁴⁶ approaches.

Eexperimental

Materials and instruments

All chemicals and reagents, including aldehydes, amines, ketone, phenyl acetylene, halloysite clay, toluene, tiosemicarbazide, furfural, ethanol, (3-chloropropyl) trimethoxysilan and $Cu(OAc)_2$ were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification. The progress of the organic reactions were monitored by TLC on commercial

al. reported immobilization of Pt nanoparticles on HNTs amine aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. ¹H NMR and ¹³C NMR spectra were recorded on Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. Catalyst characterization was carried out by applying various techniques including SEM/EDX, TGA, FTIR, XRD, BET and ICP-AES. FTIR spectra were obtained by employing PERKIN-ELMER- Spectrum 65 instrument. SEM/EDX analyses were recorded by a Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV. Room temperature powder X-ray diffraction patterns were obtained by using a Siemens, D5000. CuKa radiation from a sealed tube. The BET analyses were performed using BELSORP Mini II instrument. Prior to BET analyses, the samples were degassed at 423 K for 3 h. Thermo gravimetric analysis (TGA) was performed on a METTLER TOLEDO thermo gravimetric analysis apparatus with a heating rate of 10 °C min⁻¹ from 50 to 600 °C under N₂ atmosphere. The used ultrasonic apparatus for promoting the organic transformations was Bandelin HD 3200 with output power of 150 W and tip TT13. Notably, all of compounds were known and were identified by comparison of their melting point and spectroscopic data with those of reliable compounds. ¹H and ¹³C NMR spectra of chosen compounds are reported and specified as supplementary.

Cl-Functionalization of HNTs: Synthesis of HNTs-Cl

To introduce Cl functionality on HNTs, HNTs (1.2 g) was dispersed in 60 mL dry toluene and subsequently (3-chloropropyl) trimethoxysilan (4 mL) was added drop wise. The resulting mixture was subjected to ultrasonic irradiation of power 100 W for 0.5 h. The dispersed suspension was then reflux under inert (N₂) atmosphere for 24 h at 110 °C. Upon completion of the reaction, the precipitate was separated by simple filtering. The functionalized clay was obtained by washing with dried toluene repeatedly and drying at 100 °C overnight.

Incorporation of thiosemicarbazide: synthesis of HNTs-T

Thiosemicarbazide (0.5 g) was added to a suspension of HNTs-Cl (1g) in dry toluene (50 mL) in the presence of catalytic amount of trietylamine (1 mL). The resulting mixture was refluxed at 110 °C for 24 h. Upon completion of the reaction, the precipitate was filtered off and washed with dry toluene repeatedly. HNTs-T was obtained after drying at 100 °C overnight.

Imine functionalization of HNTs: Synthesis of HNTs-T-F

The imine functionalization was achieved by dissolving furfural (5 mL) in the stirring suspension of HNTs-T in MeOH (50 mL) followed by refluxing for 18 h. The condensation reaction could be visually detected by changing the color of the mixture into deep yellow. Upon completion of the reaction, the resulting solid was filtered off, washed with hot MeOH repeatedly and dried at 100 °C overnight.

Introduction of Cu: synthesis of Cu@HNTs-T-F

To incorporate copper species, HNTs-T-F (2g) was suspended in toluene (50 mL) and stirred to furnish a homogeneous suspension. Subsequently, copper (II) acetate (0.4 g) was added to the suspension and the resulting mixture was refluxed for 18 h. Upon proceeding the reaction, the change in the color of the mixture from yellow into green could be observed. After the end of the reaction, the precipitate was filtered off and washed with toluene for several times.



The final catalyst, Cu@HNTs-T-F, was obtained by drying the precipitated at 100 °C overnight. The schematic procedure for the synthesis of the catalyst is depicted in Figure 1.

Results and discussion

Catalyst characterization

General procedure for A³ coupling reaction

Stoichiometric amounts of the reagents including aldehyde (1 mmol), amine (1 mmol) and phenyl acetylene (1 mmol) were mixed in H_2O . Subsequently, catalytic amount of Cu@HNTs-T-F (0.02 g) was added to the mixture and the resulting mixture was subjected to ultrasonic irradiation with power of 100 W at ambient temperature for appropriate reaction time. The progress of the reaction was monitored by TLC. Upon completion of the reaction, Cu@HNTs-T-F was simply separated by filtration. The filtrate was concentrated to furnish a precipitate which was subsequently purified by column chromatography or recrystallized from hot EtOH. Notably, the recovered catalyst was washed with the mixture (1:1) of H_2O /EtOH and dried at 90 °C overnight for reusing in successive reaction runs.

The SEM/EDX images of Cu@HNTs-T-F are shown in Figure 2. As obvious, in the hybrid catalyst the tubular morphology of the pure HNTs is still observable. However, in comparison to pure HNTs (Figure 1 in supporting information), the catalyst showed more aggregated morphology. This can establish that functionalization of HNTs and incorporation of copper species affects the morphology of HNTs. This observation can be attributed to the successful functionalization of HNTs and electrostatic interactions of hetero-atoms in the functionality with copper species.

The EDX analysis of the catalyst indicates the presence of Si, Al and O atoms, which can be the representative of HNTs framework. Moreover, the presence of C, N, O and S can confirm the incorporation of organic motifs, i.e. furfural and thiosemicarbazide. Finally, the observation of Cu atom in EDX analysis can confirm the successful immobilizing of copper spices.



Figure 1. The possible formation process of Cu@HNTs-T-F catalyst

New Journal of Chemistry Accepted Manuscript

DOI: 10.1039/C7NJ02272G







Figure 3. The TEM image of fresh Cu@HNTs-T-F

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To further characterize the catalyst, the TEM images of Cu@HNTs-T-F was recorded, Figure 3. As shown in Figure 3, the tubular morphology of pure HNTs is preserved upon functionalization and copper incorporation.

The FTIR spectra of HNTs-T-F and Cu@HNTs-T-F are illustrated in Figure 4. Both spectra exhibited bands at 3705 cm⁻¹ and 3685 cm⁻¹ which are the representative of internal and external hydroxyl groups of HNTs framework. Additionally, the characteristic bands of Al-O-Si vibration and the interlayer water can be observed at 561 cm⁻¹ and 1656 cm⁻¹ respectively. The presence of bands at 2972 cm⁻¹ and 1085 cm⁻¹ which are the representative of $-CH_2$ stretching and Si–O stretching, respectively can confirm the successful attachment of (3chloropropyl) trimethoxysilan.³⁰ The observed band at 1383 cm⁻¹ can be attributed to C=S group. Two bands at 1564 cm⁻¹ and 1442 cm⁻¹ can be assigned to the asymmetric and symmetric vibrations, respectively, of the acetate ions and confirm the incorporation of copper. Furthermore, the band at 1656 cm⁻¹ is representative of imine functional group. according to the literature, the shift of imine band to lower wavelength can be due to the coordination to copper.⁴⁷

The XRD pattern of Cu@HNTs-T-F was recorded and compared with that of pure HNTs, Figure 5. As shown, the characteristic peaks of HNTs can be observed at 8°, 12°, 20°, 25°, 35°, 54° and 62.8° (JCPDS No. 29-1487). The obtained XRD pattern is in good accordance with the previously reported patterns for HNTs in the literature ^{10, 13}. The comparison of the XRD patterns of the catalyst and pure HNTs showed that both patterns were

identical and the catalyst exhibited the characteristic peaks of HNTs. This observation established that the introduction of functionalities to HNTs and incorporation of copper species did not induce the collapse of HNTs framework. This was further confirmed by BET analysis (*vide infra*). Notably, the unchanged interlayer distances of Cu@HNTs-T-F implied that the intercalation of organic motifs and copper species did not take place within the interlayer of HNTs, but on the surface and the edges of the HNTs tubes. This fact was previously observed and reported by Kepert et al¹³.

Notably, in XRD pattern of Cu@HNTs-T-F no distinguished peak was detected for copper. According to the literature, this observation can be attributed to the low amount of copper as well as its high dispersion ⁴⁸.

The TGA thermogram of Cu@HNT-T-F, Figure 6, exhibited four degradation stages over the range of 50-600 °C. The first degradation stage can be attributed to the loss of absorbed water. The next two degradation stages can be observed at 300 and 370 °C and can be assigned to the thermal decomposition of organic functionalities.



Figure 4. The FT-IR spectra of (a) HNTs-T-F (b) Cu@HNTs-T-F

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Figure 5. The XRD pattern of Cu@HNT-T-F and pure HNTs

The final degradation stage can be detected at about 500 °C, which can be due to the dehydroxylation of the matrix. Notably, the TGA thermogram of Cu@HNT-T-F is different from that of pure HNTs, Figure 6, in which only two degradation stages were reported for loss of water (about 200 °C) and the rearrangement of ions in the metakaolin state (about 500 °C) ⁴⁹⁻⁵⁰. This observation confirmed that functionalization of HNTs and incorporation of copper can alter the TGA of the pure HNTs and more degradation stages were observed in thermogaram of the catalyst compared to that of pure

HNTs, which can be attributed to the degradation of functionalities. TGA analysis was also applied for estimating the content of organic functionality in Cu@HNT-T-F. This value was calculated to be about 19.6 wt%. To calculate the content of copper in the catalyst, the digestion was accomplished in concentrated hydrochloric and nitric acids solution. Subsequently, the analysis of the obtained extract was performed by using ICP-AES. Using this method, the content of copper was estimated to be about 4 wt%.



Figure 6. The TGA analysis of pure HNTs (a) and Cu@HNT-T-F (b)

Nitrogen adsorption–desorption isotherm of Cu@HNT-T-F was obtained to study the textural features of the catalyst, Figure 7. As depicted, the shape of the isotherm is of the type II nitrogen adsorption–desorption isotherms with H3 hysteresis loops ¹³ and confirms the porous structure of the catalyst. In Table 1, the textural properties of Cu@HNT-T-F is tabulated and compared with

that of HNTs. As obvious, upon fictionalization and copper incorporation, the textural properties of the catalyst changed remarkably and average pore diameter, specific surface area and total pore volume increased in Cu@HNT-T-F. According to the previous reports, this observation can be attributed to the presence of copper species on the surface of HNTs⁵¹.



Figure 7. Nitrogen adsorption-desorption isotherms of the catalyst

Table 1. Textural properties of the catalyst and pure HNTs

Sample	$S_{BET} (m^2 g^{-1})$	Average pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
Cu@HNT-T-F	88.6	35.5	0.78
HNTs	51	15.2	0.19

Computational study

As it was discussed earlier, the detailed information about the surface chemistry of HNTs and their functionalized moieties plays an important role in design of immobilization behavior of nanoparticles to improve their performance and extend their applications $^{26-29}$. In this light, we concentrated on the quantitative description of structural and electronic features of interactions between copper acetate (denoted as Cu(OAc)₂) and thiosemicarbazide functionalized HNTs modified with furfural (denoted as HNTs-T-F) *via* density functional theory (DFT) ⁴⁵ and quantum theory of atoms in molecules (QTAIM) ⁴⁶ approaches.

In this respect, we have designed an appropriate model for HNTs-T-F ligand and its complex with copper acetate, (illustrated in Scheme 2). As it is depicted in scheme 2, two coordination modes were designed to describe the metal-ligand interactions in Cu@HNTs-T-F complex model, denoted as Cu@O-HNTs-T-F (copper coordinates to oxygen of furfural ring) and Cu@S-HNTs-T-F (copper coordinates to sulfur of thiosemicarbazide compound), respectively. It is worthwhile to note that the proposed structural model for HNTs as 1:1 layered aluminosilicates can be considered as an effective model for comparative investigation of metal-ligand interaction strength.



Scheme 2. The designed model for HNTs-T-F and its two coordinating modes with copper acetate, denoted as Cu@O-HNTs-T-F and Cu@S-HNTs-T-F, respectively

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DOI: 10.1039/C7NJ02272G Journal Name



Figure 8. The energy-minimized structure of HNTs-T-F ligand, Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes obtained at M08HX/6-31G* level of theory. Note that M08HX/6-311+G** calculated values of bond orders (bond lengths) for some key bonds in the coordination sphere of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes have been reported.

More importantly, this model has a reliable comprise between accuracy and time saving efficiency of computational procedure ⁵²⁻⁵⁴. In the first step, we determined the optimized structure of HNTs-T-F and two Cu@O-HNTs-T-F, Cu@S-HNTs-T-F complexes at M08HX/6-31G* level of theory.

The harmonic frequency analysis was used to confirm the found structures correspond to minima. It is noteworthy to state that M08HX functional has been introduced as a modern hybrid meta-GGA (generalized gradient approximation) exchange-correlation functional combined with Hartree-Fock exchange contribution ⁵⁵. In the case of copper, the effective core potentials (ECP), LANL2DZ, were used together with the accompanying basis set to describe the valence electron density ⁵⁶. All DFT computations were performed using GAMESS suite of programs ⁵⁷.

The optimized geometry of HNTs-T-F and two Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes calculated at M08HX/6-31G* level of theory have been shown in Figure 8. Furthermore, we reported M08HX/6-311+G** bond orders and bond lengths calculated values for some key bonds in the coordination sphere of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes. The comparative assessment of the bond order calculated values in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes indicate that the Cu-N interaction strength in Cu@O-HNTs-T-F complexes is higher than Cu-O and Cu-S in the Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes (0.82, 0.61 and 0.43 for calculated Cu-N, Cu-O and Cu-S bond order values in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes, respectively).

This comparative analysis demonstrates that copper acetate has a more tendency to bind with nitrogen than oxygen of furfural and sulfur of thiosemicarbazide. On the other hand, to investigate the variation of bond orders through the complexation, we reported the M08HX/6-311+G** calculated values of some selected bond orders (bond lengths) in ligand, Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes in Table 2.

The comparison of bond order calculated values in HNTs-T-F ligand with its corresponding bonds in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes, reveals that the bond order of C-O in furfural ring and also C-N and C-S of thiosemicarbazide decreases through complications in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes that is in a reversed trend with the variation of calculated bond distance values. This character can be mainly imputed to the donation of shared electrons from these chemical bonds to copper ions that also confirm by reported FT-IR spectroscopic data. In the next step, we concentrated on the computational modeling of the solvent effect in the synthesis of Cu@HNTs-T-F nanocatalyst. In this respect, we evaluated comparatively the bond orders of Cu-N, Cu-O and Cu-S in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes, in the presence of toluene and ethanol as solvents via polarized continuum model (PCM) 58. It should be noticed that better immobilization and smaller size of copper NPs on functionalized HNTs have been observed in toluene solution in comparison with ethanol ^{47, 59}. Our comparative assessment on M08HX/6-311+G** calculated bond orders of Cu-N, Cu-O (in Cu@O-HNTs-T-F complex) and Cu-S (in Cu@S-HNTs-T-F complex) in toluene and ethanol

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solution phases confirmed that Cu-N interaction in Cu@O-HNTs-T-F complex is stronger than Cu-O and Cu-S in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes (as was reported in Table 3).

Table 2.

The calculated values of some selected bond orders (bond lengths) in ligand, Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes obtained at M08HX/6-311+G** level of theory. Note that in Fig.7, we displayed the selected bonds in the optimized structure of HNTs-T-F ligand.

	Free ligand	Complex
bonded atoms		
Cu@O-HNTs-T-F Complex		
C-O	0.938(138.5 pm)	0.844(1.40.6 pm)
C-N	0.970(128.3 pm)	0.826(149.5 pm)
Cu@S-HNTs-T-F Complex		
C-S	1.184(176.7 pm)	1.136(179.5 pm)
C-N	0.970(128.3 pm)	0.942(135.4 pm)

Table 3.

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The obtained values of Cu-N, Cu-O and Cu-S bond orders in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes in toluene and ethanol solution phases, calculated at M08HX/6-311+G** level of theory *via* PCM approach

	Cu-N Cu@O-HNTs-T-F	Cu-O Cu@O-HNTs- T-F	Cu-S Cu@O-HNTs-T-F
Foluene	0.932	0.717	0.511
Ethanol	0.878	0.695	0.472

More importantly, Cu-N bond order in Cu@O-HNTs-T-F complex has larger calculated value in toluene solution in comparison with those calculated in ethanol and so approves the previously reported preference of toluene as solvent rather than ethanol in the synthesis of HNTs catalysts ^{47, 59}. On the other hand, to rationalize and quantify the metal-ligand interaction strength we assessed the topological properties of electron densities at the optimized structure of Cu@HNTs-T-F complex models *via* QTAIM method ^{46, 60}. In this line, we applied the calculated M08HX/6-311+G** wave function files for the optimized structures of Cu@O-HNTs-T-F and

Cu@S-HNTs-T-F complexes as inputs to AIM2000 program package 61 . In Table 4, we reported the calculated values of some QTAIM reliable indicators including electron density ($\rho_{-}b$), its laplacian ($\nabla^2 \ \rho_{-}b$), electronic kinetic energy density (G_b), electronic potential energy density (V_b), total electronic energy density (H_b), $|V_{-}b|$ [IG_b and delocalization index (DI) for some selected critical points in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes. We also displayed the QTAIM molecular graphs of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes including all bond and ring critical points and their associated bond paths in Figure 9.

As it is reported in Table 4, the small calculated values of electron density and delocalization index in conjunction with the positive values of $\nabla^2 \rho_b$ and small negative values of Hb and also $1 < |V_b| \equiv G_b < 2$ calculated values can be attributed to the nature of semi covalent-electrostatic interactions at Cu-N, Cu-O and Cu-S BCPs⁶². However, comparison of the calculated electron density and delocalization index values of Cu-N, Cu-O and Cu-S BCPs in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes reveals that interaction of copper cation with nitrogen is stronger than oxygen of furfural and sulfur of thiosemicarbazide.

Based on the concept of hard and soft acids and bases (HSAB) theory, we can state that Cu²⁺ as a soft acid should bind with more tendency to sulfur atom as a soft base than nitrogen atom as a hard base that in an inverse trend with our calculated results. In this context, it should be noticed that HSAB theory only assessed the electronic effects of interactions with no consideration on the steric and structural features of coordination. So, in order to assess the coordination properties of copper(II) complexes with NSO ligands, the electronic properties in conjunction with the structural aspects of complexation should be considered. In x-ray single crystal structure of these complexes, it has been observed that in the unit cell-one molecule, there are several coordination modes and geometries so that SNO ligands can act as a bidentate ligand with N,O coordination sites with square planar geometry and also as a tridentate ligand with N, S and O coordination sites and distorted square pyramidal geometry⁶³⁻⁶⁶.

Another important electronic feature that can be deduced *via* concise analysis of QTAIM molecular graphs of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes is the formation of N-H---O-C and C-H---O-C intra-molecular interactions between acetate group and HNTs-T-F ligand in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes, respectively. The QTAIM calculated values of ρ_{-} b (and $\nabla^{2}2 \rho_{-}$ b) for N-H---O-C and C-H---O-C bond critical points have been obtained 0.040au (0.142au) and 0.020au (0.075au), respectively. More importantly, it can be seen that N-H---O-C and C-H---O-C intra-molecular bondings lead to form additional rings with the requisite ring critical points in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes (with 0.037au and 0.013au electron density values, respectively) and consequently can stabilize metal-ligand interactions electronically.

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DOI: 10.1039/C7NJ02272G Journal Name



Figure 9. QTAIM Molecular graph of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes obtained by topological analysis of M08HX/6-311+G** electron density function. Bond Critical Points: green circles; Ring Critical Points: red circles; Bond Paths: grey lines.

Table 4.

Mathematical properties of BCPs associated to some selected bonds in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes. The properties have been obtained *via* QTAIM analysis on M08HX/6-311+G**calculated wave function of electron density.

	Pb	$\nabla^{2} \rho_{b}$	Gb	Vb	Hb	V _b /G _b	DI	
Cu@O-HNTs-T-F Complex								
Cu-N BCP	0.159	0.653	0.244	-0.325	-0.080	1.330	0.966	
Cu-O BCP	0.090	0.418	0.139	-0.175	-0.035	1.252	0.318	
Cu@S-HNTs-T-F								
Complex	-							
Cu-S BCP	0.065	0.105	0.050	-0.074	-0.023	1.476	0.548	
Cu-C BCP	0.140	-0.064	0.113	-0.184	-0.070	1.615	0.740	

Catalytic activity

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To study the catalytic activity of the catalyst, the A³ coupling reaction, which is an important coupling reaction in organic chemistry, was selected as a model chemical reaction. Initially, to confirm the necessity of the use of the catalyst, the reaction of benzaldehyde, phenyl acetylene and morpholine as a model reaction was performed in the absence of the catalyst. The result indicated that the presence of the catalyst is essential for obtaining the desired product. Subsequently, in attempt to disclose a green procedure for the synthesis of propargylamine, the model reaction was performed under ultrasonic irradiation and the results compared with those of obtained under solvent-free, refluxing and stirring condition. The results established that the reaction rate of the reaction performed under ultrasonic-assisted procedure was remarkably lower than those of other methodologies. More precisely, the model reaction under ultrasonic irradiation of power 100 W in the presence of 0.02 g catalyst in water completed in 15 min to furnish the desired product in excellent yield (96 %), while the rates of this reaction under reflux and stirring condition in water and the presence of the same amount of the catalyst or solvent-free condition were 45 min, 60 min and 50 min respectively. Moreover, the yields of the model product under solvent-free, refluxing and stirring condition were lower, 90, 92 and 88% respectively. Hence, using ultrasonic irradiations was found as a best methodology and the reaction condition was then optimized by altering the reaction variables including solvent, catalyst amount and the power of ultrasonic irradiation (Figure 10). As obvious, the optimized solvent, catalyst amount and ultrasonic power were found to be: water, 0.02 g and 100 W respectively. According to the literature ^{21, 67-68}, the effect of ultrasonic irradiation can be

explained according to the cavitation phenomena 69-73. That is, formation, growth and collapse of the cavities which led to the formation of spots with high temperatures and pressures. This can concentrate high amount of energy from the conversion of kinetic energy of liquid motion into heating of the contents of the cavities ⁷⁴. Notably, ultrasonic irradiation not only can enhance the rate of the chemical reactions but also²¹ influence the reaction pathway and promoting chemical reactivity ⁷⁴. In the next step, the generality of this procedure was examined by using diverse range of aldehydes with electron donating, electron withdrawing groups as well as heterocyclic aldehydes for the synthesis of various propargylamine derivatives (Table 5). Gratifyingly, all substrates tolerated the reaction to furnish the corresponding products in excellent yields in a very short reaction times (10-25 min). These results clearly established the broad substrate scope of this protocol. To elucidate the merit of Cu@HNTs-T-F and our ultrasonic-assisted protocol, the efficiencies of previously reported methodologies for promoting the model reaction were compared with that of Cu@HNTs-T-F (Table 6). As obvious, various catalysts such as Cul, CuCN and Cu₂O-ZnO have been used for catalyzing this reaction under different reaction conditions. Comparing the yield of the model product, it can be seen that CuNPs/Mag Silica, Nafion-NR50 and CuNPs/TiO₂ exhibited inferior catalytic activities. Moreover, the reaction times reported for these cases were very longer than Cu@HNTs-T-F and the reactions proceeded at elevated temperatures. In the cases of Cul, h-Fe₂O₃@DA/Ag, Cu₂O-ZnO and CuCN comparative yields were reported (using CuI led to slightly higher yield). However, comparing the reaction conditions indicated that Cu@HNTs-T-F furnishes the desired product in very shorter reaction times. Furthermore, except Cul, all catalysts required heating for promoting the reaction.



Figure 10. Effects of loading of catalyst, duration of reaction and solvent for the synthesis of propargylamine

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Table 5.

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Synthesis of three-component reaction of derivatives aldehyde and ketone, secondary-amines and terminal alkynes catalyzed by Cu@HNTs-T-F ^a [Ref] ¹⁻⁷

R ¹	R ²	R ³	R ⁴	R ⁵	Product	Time (min)	Yield ^t (%)
1a: C ₆ H ₅	н	3a: -(CH	2)5-	4a	5a	15	95
1b: <i>p</i> -Cl-C ₆ H ₄	Н	3a		4a	5b	12	93
1c: <i>p</i> -NO ₂ -C ₆ H ₄	Н	3a		4a	5c	15	90
1d: <i>p</i> -Me-C ₆ H ₄	Н	3a		4a	5d	17	91
1e:p-MeO-C ₆ H ₄	Н	3a		4a	5e	10	95
1f: <i>o</i> -OH-C ₆ H ₄	н	3a		4a	5f	10	95
1g: furfuryl	Н	3a		4a	5g	15	87
1h: 1-naphtyl	Н	3a		4a	5h	20	90
1a	Н	3b:-(CH ₂) ₂ -O-	-(CH ₂) ₂ -	4a	5i	12	97
1b	Н	3b		4a	5j	12	90
1c	Н	3b		4a	5k	15	89
1d	Н	3b		4a	51	12	90
1e	н	3b		4a	5m	10	93
1f	Н	3b		4a	5n	10	94
1g	Н	3b		4a	50	15	86
1i: <i>m</i> -NO ₂ -C ₆ H ₄	Н	3b		4a	5	17	89
1a	Н	$3c:C_2H_5$	C_2H_5	4a	5q	20	85
1j: H	Н	3a		4a	6a	15	90
1j	Н	3b		4a	6b	10	88
1j	Н	3c		4a	6c	15	90
1k: C ₆ H ₁₁	Н	3a		4a	6d	20	79
1k	Н	3b		4a	6e	17	85
1k	Н	3c		4a	6f	22	80
1I: -(CH ₂) ₂ -Me	н	3a		4a	6g	30	90
11	н	3b		4a	6h	25	94
11	н	3c		4a	6i	25	90
2a: -(CH) ₅ -		3a		4a	6j	25	90
2a		3b		4a	6k	20	92
2a		3c		4a	61	30	88
2a		3a		4b: <i>p</i> -Me-C ₆ H₄	6m	25	89
2a		3b		4c: <i>p</i> -F-C ₆ H ₄	6n	30	90

^a Reaction conditions: aldehydes 1a-k (1 mmol) or aliphatic ketone 2a (1 mmol), amines 3a-c (1.1 mmol), alkynes 4a-c (1.2 mmol), H₂O (20 ml) and Cu@HNTs-T-F (0.02 g) under ultrasonic irradiation (100 W) at room temperature. ^b Isolated yield.

Table 6.

Comparison of Cu@HNTs-T-F with other recently reported acid catalysts for the synthesis of propargylamine (Scheme 1)

Entry	Catalyst amount	Reaction conditions (solvent/ temperature)	Time (min)	Yield (%)	Ref
1	Cul (15 mg)	H ₂ O/ r.t./ U.S	45	98	81
2	Cu@HNTs-T-F (20 mg)	H ₂ O/ r.t./ 100 W	15	96	This work
3	h-Fe ₂ O ₃ @DA/Ag (10 mg)	S.F./ 90 °C	60	96	82
4	Cu ₂ O-ZnO (10 mg)	S.F./ 100 °C	60	95	76
5	CuCN (2 mol%)	[bmim]PF ₆ / S.F./ 120 °C	120	95	83
6	CuNPs/TiO ₂ (0.5 mol%)	S.F./ 70 °C	420	91	84
7	Nafion-NR50 (350 mg)	CH ₃ CN/ 70-80 °C/ N ₂ atm	300	85	32
8	CuNPs/MagSilica (10 mg)	S.F./ 100 °C/ under air	60	85	85

Reaction mechanism

The plausible reaction mechanism is illustrated in Scheme 3. As depicted, the catalyst can activate the terminal C-H bond of phenyl acetylene through formation of Cu-acetylide as an intermediate. The catalyst can also accelerate the formation of imine derived from reaction of amine and aldehyde by activation of carbonyl group. The desired propargylamine can be achieved through reaction of Cu-acetylide and imine.

Catalyst reusability

One of the most important features of a heterogeneous catalyst is the capability of simple recovery and reusing. To study the reusability of Cu@HNTs-T-F, the model reaction was carried out in the presence of the fresh and recovered catalyst. Precisely, the yield of the model reaction was investigated for short reaction intervals between 2-12 min. After the first reaction run, the catalyst was separated by simple filtration and washed with the mixture (1:1) of H₂O/EtOH and dried at 90 °C overnight and subjected for the next reaction run. The yields of the model product in the presence of the fresh and reused catalysts were compared, Figure 11. The results clearly indicate that the catalyst preserved its catalytic activity upon reusing and only a negligible loss of catalytic activity was detected.

To study the stability of the reused catalyst and to see whether the recovery and reuse of the catalyst can affect the morphology and composition and phase of the catalyst, the reused catalyst was characterized by FTIR, TEM, XRD, SEM and EDX. In Figure 12 the FTIR spectra of both fresh and reused catalysts are depicted. As shown in Figure 12, the FTIR spectra of both catalysts are almost identical, indicating that the structural features of the catalyst did not altered upon reusing. In Figure 13 the XRD patterns of fresh and reused catalysts are compared. As illustrated, both fresh and reused catalysts exhibited the characteristic peaks of HNTs, implying that reusing the catalyst did not diminish the tubular structure of HNTs and the reused catalyst preserved its structure. Next, to study the effect of the reuse and recovery on the morphology of the catalyst, the SEM image of the reused and fresh catalysts were compared, Figure 14. It was found that both fresh and reused catalysts possessed almost similar morphology in which both aggregates and rod like morphologies could be detectable. This observation clearly established that the reuse of the catalyst would not cause any remarkable change on the morphology of the catalyst. Moreover, the EDX analysis of the reused catalyst, Figure 14, showed Si, Al, O atoms, which are representative of HNTs structure as well as S, C and N, which could be attributed to the organic functionality and Cu atom. This can prove that the reused catalyst consisted of both organic functionality and copper (as it was further confirmed by ICP-AES analysis), indicating that reuse of the catalyst did not result in the detachment of the organic moiety. Finally, the TEM image of reused catalyst was obtained, Figure 14, and compared with that of the fresh catalyst, Figure 3. The similarity of both images could be considered as another proof for the stability of the reused catalyst. All these analyses can confirm that the catalyst was stable upon reusing and can be reused for the successive reaction runs.

To investigate the leaching of the copper species and elucidate whether the catalysis is heterogeneous, quenching experiment was performed by filtering the reaction mixture and studying the catalytic activity of the filtrate. It was found that the reaction did not proceed in the filtrate, indicating the suppressed leaching of the copper species. This finding was also confirmed by using ICP-AES analysis, which established almost no leaching of copper.



Scheme 3. Plausible mechanism for the synthesis of propargylamine by Cu@HNTs-T-F

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Figure 11. Reusability of the Cu@HNTs-T-F catalyst in A³ Coupling



Figure 12. The FTIR spectra of fresh Cu@HNTs-T-F (a) and after four runs (b)

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Figure 13. The XRD patterns of fresh Cu@HNTs-T-F (a) and after four runs (b)



Figure 14. The SEM (a), TEM (b) and EDX (c) images of Cu@HNTs-T-F catalyst after four runs

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Spectral data for selected compounds

1-(1,3-diphenylprop-2-ynyl)piperidine (Table 5, 5a): Pale yellow oily liquid; ¹H NMR (400 MHz, CDCl₃, ppm) δ 1.45-1.49 (m, 2H), 1.58-1.65 (m, 4H), 2.59 (t, 4H), 4.81 (s, 1H), 7.31-7.40 (m, 6H), 7.53-7.55 (m, 2H), 7.65-67 (d, *J*=7.6 Hz, 2H).

1-(1-(naphthalen-3-yl)-3-phenylprop-2-ynyl)piperidine (Table **5, 5h):** Yellow oil; ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.47-1.51 (m, 2H), 1.60-1.67 (m, 4H), 2.64 (t, 4H), 4.97 (s, 1H), 7.36-7.40 (m, 3H), 7.48-7.52 (m, 2H), 7.58-7.61 (m, 2H), 7.79 (dd, $J^1=J^2=8.4$ Hz, 1H), 7.85-7.91 (m, 3H), 8.11 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) d 24.4, 26.2, 50.8, 62.5, 86, 88.1, 123.3, 125.8, 125.9, 126.7, 127.2, 127.5, 127.7, 128.1, 128.12, 131.8, 132.9, 133.1, 136.3.

N,N-diethyl-1,3-diphenylprop-2-yn-1-amine (Table 5, 5q): Pale yellow oily liquid; ¹H NMR (400 MHz, CDCl₃, ppm) δ 1.04 (m, 6H), 2.36-2.62 (m, 4H), 5.19 (s, 1H), 7.15-7.27 (m, 4H), 7.29-7.38 (m, 3H), 7.39-7.41 (m, 2H).

4-(3-phenylprop-2-ynyl)morpholine (Table 5, 6b): yellow oil; ¹H NMR (400 MHz, CDCl₃, ppm) δ 2.64-2,67 (m, 6H), 3.52 (s, 3H), 3.69-3.71 (m, 1H), 3.77-3.79 (m, 6H), 7.28-7.31 (m, 4H), 7.43-7.46 (m, 2H).

4-(1-phenylhex-1-yn-3-yl)morpholine (Table 5, 6h):Yellow oil; ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ 0.97 (m, 3H), 1.45-1.75 (m, 4H), 2.67–2.70 (m, 2H), 2.79–2.83 (m, 2H), 3.82-4.13 (m, 1H), 4.15-4.17 (m, 4H), 7.46–7.50 (m, 3H), 7.62–7.64 (m, 2H).

4-(1-(2-phenylethynyl)cyclohexyl)morpholine (Table 5, 6k):Pale yellow oily liquid; ¹H NMR (400 MHz, CDCl₃, ppm) δ 1.28-1.30 (m, 1H), 1.52 (m, 2H), 1.63-1.67 (m, 3H), 1.73 (br.s, 2H), 2.03-2.05 (m, 2H), 2.74 (br.s, 4H), 3.78 (br.s, 4H), 7.27 (m, 3H), 7.44-7.45 (m, 2H), ¹³C NMR (100 MHz, CDCl₃, ppm) δ 22.7, 25.7, 35.4, 46.6, 58.8, 67.4, 86.4, 89.8, 123.4, 127.7, 128.1, 131.7.

1-(1-(2-p-tolylethynyl)cyclohexyl)piperidine(Table5,6m):Yellow oil;¹H NMR (400 MHz, CDCl₃, ppm) δ 1.39-1.93 (m,16H),2.17-2.20 (m, 2H),2.53 (s, 3H),2.73-2.83 (m, 2H),7.26-7.27 (m, 3H),7.46-7.48 (m, 2H);¹³C NMR (100 MHz, CDCl₃, ppm) δ 21.32,23.4,24.4,25,26.7,37.6,47.9,58.8,85.4,92.1,123,127.6,128.3,133.

4-(1-((4-fluorophenyl)ethynyl)cyclohexyl)morpholine (Table 5, 6n): Yellow oil; ¹H NMR (400 MHz, DMSO- d_6 , ppm) δ 1.26-1.34 (m, 1H), 1.57-1.62 (m, 2H), 1.69-1.78 (m, 3H), 1.80-1.86 (m, 2H), 2.00-2.02 (m, 2H), 2.78 (s, 4H), 3.70 (br.t, *J* = 4.2 Hz, 4H), 6.97-7.00 (t, *J* = 8.6 Hz, 2H), 7.32-7.40 (m, 2H).

Conclusions

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In summary, a novel catalyst has been developed by functionlization of HNTs with (3-chloropropyl) trimethoxysilan, thiosemicarbazide and furfural and incorporation of copper species. The utility of this catalyst for A^3 and KA^2 coupling reactions of aldehydes and ketone, phenyl acetylene and amines for synthesis of corresponding propargylamines under ultrasonic irradiation was confirmed. Besides excellent catalytic activity, the catalyst was reusable and could be recovered and reused up to four reaction runs. Notably, the introduced functionality of the HNTs support could effectively immobilize the copper species and suppress its leaching. Broad substrate scope, simplicity of the procedure, the green and environmentally benign nature of the protocol as well as

the excellent reusability of the catalyst is the merits of this methodology.

On the other hand, we computationally assessed the interaction of copper acetate with HNTs-T-F *via* the design of two coordination modes in Cu@HNTs-T-F complex model. The comparative analysis of calculated bond orders and all QTAIM indicators demonstrates that copper acetate has a more tendency to bind with nitrogen than oxygen of furfural and sulfur of thiosemicarbazide moieties which can predict and interpret the immobilization behavior of copper acetate on functionalized HNTs. Moreover, concise analysis of QTAIM molecular graphs of Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes shows the intra-molecular interactions between acetate group and HNTs-T-F ligand in Cu@O-HNTs-T-F and Cu@S-HNTs-T-F complexes that leads the formation of additional ring critical points with a considerable electronic stabilizing effect on metal-ligand interaction.

Acknowledgements

The authors appreciate partial financial supports from Alzahra University and Iran Polymer and Petrochemical Institute. MMH is also thankful to Iran National Science Foundation for the Individual given grant. S. Sadjadi and M. M. Heravi are thankful to Iran National Science Foundation (INSF) for supporting this research under contract No. 95834576.

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