Catalysis

Highly Stable Copper Nanoparticles Linked to Organic Frameworks as Recyclable Catalyst for Three-Component Click Cycloaddition in Water

Sadasivan P. Prakash[a, b] and Karical R. Gopidas*[a, b]

Synthesis, characterization and catalytic applications of highly stable copper-nanoparticles linked to aromatic frameworks are reported. Synthesis of these nanoparticles was achieved in a one-pot reaction which involved the simultaneous reduction of CuCl₂.2H₂O and 4,4’-biphenylene-bis-diazonium tetrafluoroborate using sodium borohydride. Copper atoms formed upon reduction of Cu ions undergo clustering, leading to the formation of copper nanoparticles. At the same time, 4,4’-biphenylene-bis-diazonium tetrafluoroborate are converted to biphenylene biradicals, which undergoes rapid addition reactions with each other and also on to the nanoparticle surfaces resulting in the formation of aromatic framework linked Cu nanoparticles. Four different types of nanoparticles were prepared by varying the concentration of the metal salts and the ligands. The structure and morphology of these materials were studied using XRD, XPS, SEM and HRTEM analysis. The materials were found to be very good catalysts for click reactions between azides and alkynes and exhibited TOF values as high as 305400 h⁻¹. They also efficiently catalyzed the one-pot click reactions involving azide precursors, sodium azide and alkyne. TOF up to 99000 h⁻¹ were observed for these reactions.

Introduction

1,3-dipolar Cycloaddition reactions involving alkynes and azides catalysed by copper is the most common and widely studied example in click chemistry.[1-5] The product of these reactions are 1,2,3-triazoles which are very resistant to moisture, oxygen and light. Click reactions have wide range of applications in various areas such as synthetic,[6, 7] supramolecular[8] and combinatorial chemistry[9] as well as in material,[9, 10] biological[11] and pharmaceutical[12] sciences. For example, 1,2,3-triazole-containing compounds show a wide range of biological activities including fungicidal,[13] antiallergic,[14] antiviral,[15] antibacterial,[16] antitumor[17] and anti-HIV[18, 19] properties.

Only a few azides are available commercially and hence, multi-step reactions are required for the preparation of complex triazoles. Therefore researchers are looking for multi-component one pot synthesis in which in situ generated azides from diazonium salts, amines, epoxides or even alkenes could be used.[19-22] Toxic side products generated during multi-step procedures and the catalysts generally have low metal contents.[23-26] In the case of Cu catalysts an important disadvantage is easy deactivation of the catalyst through oxidation. Hence preparation of stable Cu nanoparticles for catalytic applications in water is very challenging.[27-30]

Various support materials such as silica, alumina, graphene, etc. have been used extensively for the preparation of supported Cu and copper oxide nanoparticles. In most of the reported cases synthesis of the stabilizing ligands involved multi-step procedures and the catalysts generally have low metal contents.[31-33] Herein, we report novel Cu nanoparticle catalysts designated as copper nanoparticle-linked organic frameworks (CNOFs), where the metal nanoparticles are covalently linked to an aromatic framework support. The capability of copper to attain various oxidation states makes it a suitable candidate for the preparation of nanoparticles with varying composition and morphologies.[34-36] The chemical reduction of diazonium salts to ary radicals which are capable of covalent bond formation with almost any type of solid surfaces, is employed herein to construct the organic framework and to link it covalently to the Cu nanoparticle. This method has been employed to graft organic moieties on to a large number of surfaces.[37-40] Our group has also exploited this methodology to synthesize gold and palladium nanoparticle cored dendrimers and palladium nanoparticle-linked organic frameworks where the organic residues are linked to the nanoparticles by carbon-metal bonds.[41-44] In this paper we extend this strategy to synthesize CNOF, in which the copper nanoparticles are captured in the organic framework through several metal-carbon covalent bonds.

[a] S. P. Prakash, Dr. K. R. Gopidas
Photosciences and Photonics, Chemical Sciences and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIST)
Thiruvananthapuram 695 019 (India)
E-mail: gopidaskr@niist.res.in
[b] S. P. Prakash, Dr. K. R. Gopidas
Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST Campus
Thiruvananthapuram 695 019 (India)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/slct.201601127

ChemistrySelect 2016, 1, 4803 – 4813
Wiley Online Library

4803 © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
Our strategy involved the simultaneous reduction of a copper salt and a bisdiazonium tetrafluoroborate. The formation of microporous organic framework and insertion of nanoparticles into this framework could be accomplished in a one-pot reaction using NaBH₄ as reducing agent. The Cu²⁺ is reduced to Cu atoms that generate copper nanoparticles through clustering of atoms. The bisdiazonium salt upon reduction eliminates two nitrogen molecules and form highly reactive biradicals that undergo random coupling or radical radical addition reactions leading to the formation of a complex organic framework with lots of reactive radical centers capable of covalent bond formation with the growing copper nanoparticles. These two simultaneous reactions will lead to the formation of CNOF as shown in Scheme 1. Thus, our approach would permit us to synthesize CNOF in high yields in a single step. It may be noted that all the starting materials and reagents used for the preparation of CNOFs were water soluble, while the product CNOFs were completely insoluble. Hence the separation and purification of the materials were very easy.

By changing the relative concentrations of the bisdiazonium fluoroborate and Cu salt, we were able to synthesize four CNOF systems (designated here as CNOF1, CNOF2, CNOF3 and CNOF4). All the CNOFs were analyzed using different spectroscopic and microscopic techniques. The CNOFs were then evaluated for their catalytic activity towards click cycloaddition reactions in water. We also performed these reactions as a three-component, one-pot reactions wherein the azides were generated in situ from benzyl bromides or aryl diazonium salts.

**Results and Discussion**

Synthesis of CNOFs involved the simultaneous reduction of 1,4-biphenylenes-bisdiazonium fluoroborate (BPBDT) and CuCl₂·2H₂O dissolved in toluenewater (2:1) mixture by NaBH₄ in methanol. The CNOFs were obtained as black powders insoluble in almost all solvents. The samples were purified by repeated washing with water and organic solvents such as acetone, THF and CH₂Cl₂ followed by drying in vacuum. Dispersions of CNOFs in water settled within 15 minutes, whereas their dispersions in organic solvents took nearly an hour to settle. Irrespective of the density of the solvents and solubility of CNOFs in them, CNOFs always preferred the organic phase in a water-organic biphasic system.

Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) of CNOFs were carried out at a heating rate of 10 °C per minute. The results obtained are presented in Figure 1. To get the complete decomposition of the framework into CO₂ and H₂O analysis were done in the presence of atmospheric oxygen. The thermogrm of CNOF1 showed only a small weight loss of less than 0.8% up to 100 °C. This can be attributed to the evaporation of solvents adsorbed to the materials. DTA analysis shows that major exothermic reactions occur at 180 °C and 315 °C. The first peak is due to the oxidation of copper i.e. Cu(s) → Cu₂O(s) and the second peak is due to the oxidation of cuprous oxide Cu₂O(s) → CuO(s). The DTA also showed peaks at 520 °C and 790 °C. The former peak can be attributed to the combustion of organic frameworks and the latter may be due to possible phase change occurring to CuO. This phase change arises due to melting which starts around 790 °C. The thermogram shows total weight loss of 21%. Assuming complete decomposition of the organics and oxidation of Cu to CuO, we can assign the remaining 79% to CuO which would correspond to 63% Cu originally present in the CNOF1 and the remaining 37% weight was taken as due to the organic framework. CNOF2 exhibited similar behavior and analysis of TGA and DTA gave Cu wt% of 74. Thermograms of CNOF3 and CNOF4 exhibited total weight gains of 1.8% and 10.6%, respectively. A net weight gain is observed because the weight gain due to oxidation to CuO is more than the weight loss due to decomposition of the organic framework. Analysis of the results gave total metal contents of 81% and 88% for CNOF3 and CNOF4, respectively.

Further characterization of CNOFs were accomplished using FTIR, NMR and UV-Visible spectroscopies (see supporting information (SI) for IR and NMR spectrum). FTIR spectra for the CNOFs and the ligand BPBDT are shown in Figure S1 in the SI. The IR spectrum of BPBDT exhibited a band at 2274 cm⁻¹ which is characteristic of the diazo group. This band was absent in the IR spectra of all the four CNOFs, indicating the complete removal of diazonium groups. All other IR absorptions corresponding to the C–H (3033 cm⁻¹) and C–C (peaks between 1600 and 1400 cm⁻¹) vibrations present in the ligand were also present in the CNOFs. The intensities of these bands were observed to decrease with increase in the metal content. CNOF4 has the lowest peak intensity due to its low organic content.

Due to the lack of solubility in organic solvents we employed sonicated suspensions of the CNOFs in CDCl₃ for obtaining 'H NMR spectra. In Figure S2 (SI) we have compared the 'H NMR of CNOFs with that of BPBDT in D₂O. 'H NMR of BPBDT showed two sharp doublets at δ 8.64 and 8.21 ppm, as expected for 1,4-disubstituted benzene derivatives. The high δ value is due to the presence of the diazonium group. In the case of CNOFs these two sharp doublets were absent but a broad and complex band structure in the range 6.7 - 7.7 ppm could be seen. This indicates complete removal of the diazonium group and formation of a complex structure. In the case of CNOF1, which is having the highest organic content, the multiplet pattern in the aromatic region exhibited sharp peaks. As we go from CNOF1 to CNOF4 the metal content increased and the NMR signals became very broad. Broadening of NMR...
signals were observed previously in the case of nanoparticle cored dendrimers and palladium nanoparticle linked organic frameworks.\[57\] The NMR line broadening arises due to the fast spin-spin relaxation of atoms close to a metal.\[50, 66\] In the case of CNOF1 the metal content is less and the observed sharp peaks correspond to organic frameworks placed away from the metal. As the metal content increases the average distance between nanoparticles decreases and most of the framework comes under the influence of metal particles leading to a broadening of NMR signals as observed for CNOF4.

Dispersions of CNOF in toluene were sonicated for five minutes and filtered through a 0.45 μm filter pad and the resulting clear solutions were subjected to UV-Visible spectroscopy. The spectra obtained are shown in Figure 2. It can be seen from Figure 2 that none of the CNOFs exhibited the characteristic plasmon band of Cu nanoparticles at 560–590 nm. Absence of plasmon absorption is attributed to the small size of the nanoparticles (vide infra). It has been reported that plasmon absorption due to Cu nanoparticles can be seen only if the sizes of the particles are larger than 12 nm.\[67, 68\] The CNOF absorption spectra obtained showed increasing absorption in the region below 500 nm.

Powder X-ray diffraction (PXRD) analysis was carried out to confirm the presence and crystalline nature of Cu nanoparticles in the CNOFs. The results obtained are presented in Figure 3. All the four CNOFs gave intense and broad XRD peaks.
peak indicates that the metal clusters are highly crystalline. The broadness of the peaks indicates the nanosize of the particles. The Cu-containing samples exhibited diffraction peaks at 2θ angles of 43.2°, 50.4° and 74.0° with the d-spacing of 0.21 nm, 0.18 nm and 0.13 nm, which correspond to crystal facets of (111), (200) and (220), respectively (JCPDS no. 00–004-0836) of face centered cubic (fcc) structure. The crystallite sizes were calculated by using Scherrer’s equation from the width of the peak at 2θ angle of 43.2°. The average crystallite sizes are found to be 3.2 nm for CNOF1, 3.4 nm for CNOF2, 3.7 nm for CNOF3 and 4.4 for CNOF4. The PXRD contains impurity peaks arising from Cu2O at 2θ angles of 36.5° and 61.5° (JCPDS no. 03–065-3288). No peaks were present from CuO impurities. The intensities of peaks from Cu2O impurities remain unchanged even after one month. This indicates that no further oxidations were taking place and the CNOFs were highly stable. The intensity of the Cu2O peak at 36.5° increases as we go from CNOF1 to CNOF4. This can be due to decrease in the percentage of organic frameworks. This will lead to the increase in number of surface Cu atoms that can be oxidized to Cu2O.[69]

Information about the oxidation state of Cu and the nature of bonding between the framework and Cu nanoparticle in CNOF were obtained from X-ray photoelectron spectroscopic (XPS) analysis. XPS survey spectra for the CNOFs are shown in Figure S3 in SI. All the CNOFs contain the signals for Copper (75 eV for Cu 3p, 122 eV for Cu 3s, 935 eV for Cu 2p3/2, 955 eV for Cu 2p1/2, and 571 eV for Cu LM-M2), carbon (284 eV for C 1s) and oxygen (532 eV for O 1s and 980 eV for O KLL). No other characteristic signals corresponding to other atoms were present in the survey spectrum. This indicates that no other hetero atoms were present in the CNOFs.

A curve fitting program was used to deconvolute the C 1s, O 1s and Cu 2p peaks of CNOF. The C 1s peak observed in the 281–288 eV range could be deconvoluted adequately in to C–Cu (283.5 eV), C–C (284.5 eV), C–H (285.3 eV) and C–O–Cu (286.3 eV) contributions. As we go from CNOF1 to CNOF4 intensity of the C–O–Cu increases relative to the C–Cu peak suggesting that CNOF having higher metal content have more oxide content. Analysis of the O 1s peak thus revealed that the organic framework is linked to Cu through C–C or C–O-Cu bonds.

The O 1s XPS peak can be deconvoluted into two. The first peak observed at 530.28 eV can be assigned to the oxygen in the Cu2O and the second peak at 533.0 eV can be assigned to the oxygen in the Cu–O–C bonds.[48,71] As the metal content increases the intensity of Cu2O peak increases due to more Cu atoms that can get oxidized. On the other hand, the intensity of the Cu–O–C peak decreases in intensity with increase in metal content. This may be due to the decrease in the organic content which reduced the number of bonds to the framework. No peaks corresponding to CuO (529.6 eV) were observed in the O 1s XPS of any of the CNOFs.[71,72] Thus analysis of C 1s and O 1s XPS clearly indicated that the CNOF surface contains only Cu and Cu2O.

To find the oxidation state of Cu present on the nanoparticle surfaces, XPS analysis of Cu 2p were carried out and the results are shown in Figure S4 (SI). All the CNOFs have
peaks corresponding to Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} spin-orbit components. The Cu 2p\textsubscript{3/2} peak was observed between 934–936 eV and the corresponding shake-up satellite peak was seen between 944–946 eV. The Cu 2p\textsubscript{1/2} peak was seen between 954–956 eV and the corresponding shake-up satellite peak was observed between 964–966 eV. Previous studies have shown that metal nanoparticles stabilized by metal carbon covalent bonds will show M\textsuperscript{2+} peak in the XPS. Similar results are obtained for CNOFs also. Both the Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} peaks can be deconvoluted into two peaks each. The major peak (934 - 936 eV) can be assigned to Cu\textsuperscript{2+} and the minor lower energy peak (932 - 934 eV) can be due to either Cu\textsuperscript{+} or Cu\textsuperscript{0}. It is very difficult to distinguish between Cu\textsuperscript{+} and Cu\textsuperscript{0} due to the very small energy difference between them. All the peaks obtained for CNOFs were at higher energy compared to those reported for unsupported Cu nanoparticles. It is well established that binding energy will be higher for supported Cu nanoparticles, especially if the bonding between the nanoparticles and support are stronger. Thus the XPS data show that Cu nanoparticles are well bonded to the organic frameworks and not trapped in the organic frameworks.

To study the morphology of the CNOFs we have carried out SEM and HRTEM analysis. The SEM images of CNOFs show large porous structures (Figure S5-S8 (SI)). The organic frameworks generated by the random additions of bisphenylene biradicals are expected to be planar but they get attached to spherical nanoparticles from all directions leading to three dimensional structures. Since these are not soluble they aggregate and precipitate out during the reaction. The images we see in the SEM are large aggregates of CNOFs.

TEM images of CNOFs (Figure 5, see Figures S9-S12 in SI for more images) show large numbers of nanoparticles of size ≤ 8 nm embeded with in a soft material. Contours of the soft framework can be seen in all TEM images. The average particle size obtained for CNOF1 is 4.2 nm, for CNOF2 4.3 nm, for CNOF3 4.9 nm\textsuperscript{[A2]} and for CNOF4 5.7 nm (Figure 6). The values obtained were comparable with those calculated from the XRD analysis. Using this data we have calculated the number of surface Cu atoms in the CNOFs and the details are presented in the SI. No metal particles were observed outside the contours of the organic framework. Nanoparticles can be found outside the frameworks only if they are entrapped in the frameworks through non-covalent interactions. Absence of particles outside...
the contours confirms that the metal nanoparticles are co-
valently attached to the network.

To confirm the presence, composition and packing of the
copper nanoparticles, we have done selected-area electron-dif-
fraction (SAED) analysis. The results obtained are presented in
the Figure S13 in SI. SAED pattern obtained are in agreement
with the presence of copper nanoparticles. SAED pattern also
showed the peak due to the presence of Cu₂O impurities. The
intensities of such peaks are very low in the case of CNOF1 and
CNOF2. In the other two cases intensities of Cu₂O peaks are
somewhat better. As explained in the case of XRD peaks, this
can be due to increased amounts of Cu₂O on the surfaces of
CNOF3 and CNOF4 nanoparticles.

Catalytic activity of CNOFs for the click reactions

Although it is generally believed that Cu¹ is the key catalyst in-
volved in the click reaction[70] Cu with all the possible oxidation
sates are found to be catalyzing this reaction.[79–81] For example
different kinds of copper nano structures including copper,
copper oxides (both Cu₂O and CuO nanoparticles) and PVP-sta-
bilized Cu₂O nanoparticles, were recently found to catalyze
these reactions. It is generally believed that either binuclear or
mononuclear copper species is involved as the key inter-
mediate in the Cu(I) catalyzed reactions. Lack of reactivity of
disubstituted alkynes in Cu(I) catalyzed reactions indicates that
the deprotonation of the terminal alkyne plays a major role in
the generation of Cu(alkynyl) intermediate.[82] We found that
CNOF1-CNOF4 can catalyze click reactions shown in Scheme 2.
The results obtained are shown in Table 1. Table 1 shows that
TON and TOF are very high for benzylazide but somewhat low
for 4-nitrophenylazide. Click reactions between alkynes and aryl
azides are generally slow,[83] which explains the low TOF value.

Although all the CNOFs are good catalysts for the click re-
action between azides and alkynes, we did not explore these
reactions any further because only few azides are commercially
available. There are reports in the literature where click re-
actions are performed using in situ generated azides.[19, 20] Alkyl
and benzyl azides can be prepared from the corresponding hal-
ides and sodium azide (Na₃N). The generation of azide and its

---

**Table 1.** CNOF catalyzed 1,3-dipolar cycloaddition of phenylacetylene with benzyl or 4-nitrophenyl azide.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide</th>
<th>CNOF/ mol%</th>
<th>Yield/Time (%)/(h)</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>1/5.0</td>
<td>95/0.40</td>
<td>76300</td>
<td>181600</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>2/5.9</td>
<td>95/0.35</td>
<td>68400</td>
<td>207400</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>3/6.4</td>
<td>97/0.25</td>
<td>72800</td>
<td>291300</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>4/6.9</td>
<td>95/0.25</td>
<td>76300</td>
<td>305400</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>1/5.0</td>
<td>83/10</td>
<td>66600</td>
<td>6660</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>2/5.9</td>
<td>91/10</td>
<td>65500</td>
<td>6550</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>3/6.4</td>
<td>97/10</td>
<td>72800</td>
<td>7280</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>4/6.9</td>
<td>93/10</td>
<td>74700</td>
<td>7470</td>
</tr>
</tbody>
</table>

[a] Conditions: Azide (1 mmol), Alkyne (1.1 mmol), CNOF (5 mg) and water (4 mL) were stirred in aerobic conditions at 40 °C for A and at 70 °C for B. [b] Calculated through GC-MS analysis. TON = (Yield) / (100 × number of moles of surface Cu atoms in the CNOF). TOF = TON / Time.

---

**Scheme 2.** CNOF catalyzed 1,3-dipolar cycloaddition between phenylacetylene with benzyl and 4-nitrophenyl azide.
The subsequent reaction with alkynes can be thus accomplished in a one-pot reaction using azide precursor, sodium azide, alkyne and the click catalyst. Copper oxide nanoparticles and copper nanoparticles supported on carbon were reported as catalysts in these three-component click reactions.\cite{19, 77, 84, 85} We observed that the CNOFs are better catalysts for the one-pot reactions and this aspect was studied in detail using CNOF3 as catalyst.

In order to select one catalyst for this study we performed a control experiment employing benzyl bromide, sodium azide and phenyl acetylene in water at 70 °C, with CNOFs as catalyst as shown in Scheme S1. The results are presented in Table S6 (SI) which showed that CNOF3 gave the best yield. In order to optimize the reaction conditions with CNOF3 the one-pot reaction (Scheme S2) was performed under the various reaction conditions mentioned in Table S7. It can be seen from Table S7 that the reaction did not occur below 60 °C. At 70 °C the reaction was completed in 40 min whereas at 100 °C reaction was completed within 20 min. Further experiments have shown that higher temperatures are required only for the azide formation step. Once the azide is formed the CNOF3 is capable of catalyzing the click reaction at room temperature. Thus the reaction conditions could be modified as in entry 9 and 10 of Table S7. In these cases benzyl bromide/ sodium azide mixture was heated to 60 (or 70) °C, cooled to room temperature followed by addition of the alkyne and CNOF3. Stirring at RT for 30 min. gave near quantitative yields in both cases. This method is very much suited when the alkynes employed are very volatile. Heating at higher temperatures in these cases led to low yields due to loss of the alkyne by evaporation.

We have carried out several one-pot click reactions (Scheme 3) using CNOF3 as catalyst. The reaction conditions and yields are shown in Table 2. An examination of Table 2 shows that the one-pot click reactions using CNOF3 as catalyst gave excellent yields in cases studied. For most of the reactions in Table 2 yields are > 95%. With highly volatile alkynes (entries 17–19) reactions were carried out by heating the halide and NaN₃ at 70 °C, cooling to room temperature and then adding the alkyne and CNOF3 followed by stirring at RT. For these cases the time indicated in Table 2 correspond to stirring at RT. The catalyst recovered after the 5th cycle was analyzed using HRTEM. The results obtained are shown in Figure 7, which shows that the average particle size decreased from 4.9 nm to 1.9 nm. The particle size distribution also got narrowed. This means that some leaching of Cu occurs into the solution during each cycle. Comparing to Figure 5, we may suggest that leaching occurred preferentially from bigger particles so that after 5 cycles particles of nearly uniform size were formed.

**Leaching tests of the catalysts**

According to World Health Organization’s (WHO) guideline copper content of 2.0 mg L⁻¹ in drinking water is the safe limit.\cite{86} Increase in copper level in the body can generate more reactive oxygen species. These can badly affect the body and will cause various diseases.\cite{87} Apart from this toxic effect, leaching of Cu from nanoparticles into solution during the reaction is the major factor that has a detrimental effect on the catalytic activity of supported Cu catalysts.

To see if any leaching out of Cu is occurring during the reaction inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis was performed (see the experimental section). We observed 0.25 % of Cu leaching in one cycle when 5 mg CNOF3 and 1 mmol of the reactants were used for the reaction. ICP-AES analysis of the product was also carried out.
Recently reported catalysts for click reactions with high TOF include, dendrimer nano-reactor for part-per-million Cu catalyst (TON = 51000, TOF = 21200 h⁻¹), amphiphilic Cu catalyst (TON = 86000, TOF = 3600 h⁻¹) for two component click reaction and alumina supported Cu (TON = 495, TOF = 4950 h⁻¹) for three component click reactions. The TOF and TON values obtained with our catalyst for both two-component (Table 1) and three-component reactions (Table 2, Table S6 and Table S7) are comparable and even higher than the recently reported values.

It is a well-accepted principle that supported nanoparticle catalysts on supports are better than bulk metal catalysts owing to the large surface to volume ratio and the distribution of the particles on the support surface. Synthesis and applications of copper nanoparticle catalysts is reviewed recently. Cu or Cu(I) nanoparticles supported on ionic polymer, zeolite, Wyoming’s montmorillonite clay, silica, activated carbon and charcoal are reported to catalyze click reactions and hence it is very much imperative on our part to compare the CNOFs with these catalysts. In few of the above cases the catalyst preparation required harsh conditions such as heating at 500–600 °C. Cu supported on ionic polymer and zeolite required azides for the reaction and reactions were carried out in DMF:water (4:1) or methanol-water mixtures. The mol% of catalyst required was also very high in the former case. In the case of Wyoming’s clay, reaction required CH₂Cl₂ solvent. In the case of Cu on silica inert conditions such as nitrogen atmosphere is required for the successful con-

(see the experimental section). It was found that the product was not contaminated with Cu (detection limit was 0.01 ppm).
quired THF and triethylamine and the latter used dioxane as solvent. In both cases catalysts were not stable and could not be reused. Compared to all these reported cases CNOFs have several advantages. These can be synthesized easily and the one-pot reaction could be accomplished in water. The recently reported kenaf bio-cellulose based poly(hydroxamic acid) copper catalyst is highly active and works well at room temperature. However, preparation of the catalyst involves multiple steps and the click reactions are performed in methanol. In the case of CNOFs inert reaction conditions are not required, reaction times are less and product separation is very easy. These catalysts can also be reused several times.

Conclusions

In this paper we report the synthesis, characterization and catalytic applications of Cu nanoparticles covalently linked to an aromatic framework. Synthesis was accomplished in a one-pot reaction which involved NaBH₄ reduction of a bisdiazonium salt and CuCl₂. The structure and morphology of these materials were examined using XRD, XPS, SEM and HRTEM. These materials were found to catalyze the click reactions between azides and alkenes in water. We employed these materials as catalysts in the one-pot synthesis of 1,2,3-triazoles from azide precursors (halides or diazonium salts), sodium azide and alkenes and in all cases the yields were very good.

The TON and TOF values were very high compared to previously reported catalysts. Most of the previously reported catalysts were prepared using harsh reaction conditions and required organic solvent as reaction medium or inert conditions to carry out the click reaction. On the other hand, the CNOFs are prepared in one step. The CNOF catalysts were highly stable and inert conditions were not required. We observed that the CNOF catalysts could be recovered and reused several times. They work well as catalyst for the click reaction both for the benzyl azides generated from benzyl halides and for aromatic azides generated from the diazonium salts.

Supporting Information

The Supporting Information contains: Experimental section, FTIR, NMR, XPS, SEM, HRTEM and SAED of CNOFs, calculated physical data for CNOFs, results of CNOF catalyzed reactions and characterization of click reaction products.

Acknowledgements

The authors thank CSIR and the Network project CSC0125 for financial support. SPP thanks UGC for a research fellowship. We also thank SAIF KOCHI for the ICP-AES analysis.

Keywords: Click chemistry · Copper · Heterogeneous catalyst · Nanoparticles · Supported catalysts

Table 3. Three-component 1,3-dipolar cycloadditions catalyzed by CNOF3 using aromatic diazonium compounds

<table>
<thead>
<tr>
<th>Entry[a]</th>
<th>Diazonium salt</th>
<th>Alkyne</th>
<th>Yield (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>2a</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>3a</td>
<td>2b</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>3a</td>
<td>2c</td>
<td>86</td>
</tr>
<tr>
<td>4</td>
<td>3b</td>
<td>2a</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>3b</td>
<td>2b</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>3b</td>
<td>2c</td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td>3c</td>
<td>2a</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>3c</td>
<td>2b</td>
<td>86</td>
</tr>
<tr>
<td>9</td>
<td>3c</td>
<td>2c</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>3a</td>
<td>2f[c]</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Conditions: Diazonium salt (1 mmol), NaN₃ (1.1 mmol), Alkyne (1.1 mmol), CNOF3 (5 mg) and water (4 mL) were stirred in aerobic conditions at 70 °C. [b] Isolated yield. [c] Reaction at 45 °C.

Figure 7. a) HRTEM of recovered CNOF3 and b) Core-size histograms (F = frequency).

Submitted: August 12, 2016
Accepted: September 12, 2016