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Graphical Abstract

Ag-grafted covalent imine network material for one-pot three-component coupling and hydration of nitriles to amides in aqueous medium

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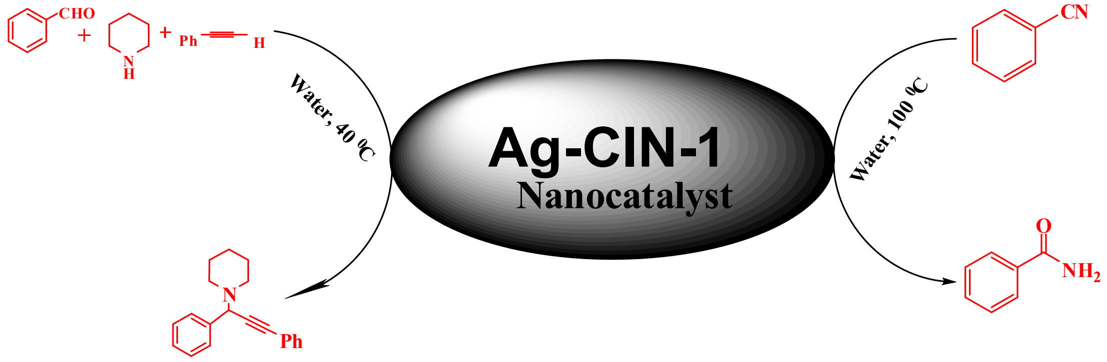
Silver grafted porous covalent imine network material (Ag-CIN-1) has been designed via a simple chemical route and it has been successfully employed as catalyst for the hydration of nitriles to amide and A^3 coupling reaction of an alkyne, an amine and an aldehyde in water.



Ag-grafted covalent imine network material for one-pot three-component coupling and hydration of nitriles to amides in aqueous medium

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Abstract

Nitrogen rich porous covalent imine network material (CIN-1) has been successfully employed for grafting silver nanoparticles (Ag NPs). The Ag NPs grafted CIN-1, Ag-CIN-1 has been characterized by elemental analysis, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), UV-vis diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA) and EPR spectroscopic studies. Ag-CIN-1 acts as a truly heterogeneous catalyst in the hydration of nitriles to amide and A^3 coupling reaction between the alkyne, amine and aldehyde to produce propargylamines by using water as a green solvent.

Keywords: porous material, 1,4-piparazinedicarbaldehyde, silver nanoparticles, nitrile, amide, A^3 coupling.

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Introduction

High surface area porous organic polymers (POPs) , which can be designed through a wide range of chemical reactions between the reactive functional organic moieties of the precursor organic monomers are attracting increasing interests over the years.[1–4] Synthesis of these microporous organic polymers with a rational design at the molecular level using cheap and simple processes are highly desirable. These porous materials are primarily employed as gas storage,[5,6] and heterogeneouscatalysis.[7,8] A large number of POPs has been invented till date like, polymers of intrinsic micro porosity[9] and conjugated microporous polymers[10] for efficient and robust heterogeneous catalysts because of their synthetic diversity, presence of a wide range of donor sites in the framework and high mechanical stability together with high surface areas.[11] Especially, incorporation of an active functionality bearing nitrogen-containing groups in the polymeric network is very demanding as it could help to bind an active metal sites at the surface of the material, and thus to enhance the catalytic performance as well as the stability of the supported materials.[12] Nitrogen-rich covalent organic frameworks can act as a catalytic support to immobilize an active metal and thus immobilized metal sites in heterogeneous molecular catalysts based on polymeric porous materials bearing active legend moieties within the framework are very demanding.[13]

Due to strict environmental regulations environmentally benign, efficient, economical and green synthesis routes for the synthesis of organic fine chemicals have become more demanding today. Over the past decade, transition metal catalyzed multi-component reactions are a powerful synthetic tools to access complex structures from simple precursors via one-pot synthetic pathways. In this context, the three-component coupling of aldehydes, alkynes, and amines (A^3 coupling) is one of the best examples of such a process and this has received much attention in recent times.[14] During the last few decades, there are several reports on highly efficient A^3-coupling in organic media, water, ionic liquid, or under solvent-free conditions catalyzed by copper, silver, gold, iron, nickel or iridium based catalysts via catalytic C–H activation to afford various propargylamines.[15] The resultant propargylamines are versatile intermediates for organic synthesis[16] and important structural elements of natural products, making agrochemicals and potential drug molecules.[17]

In this context it is also pertinent to mention that hydration of nitriles into the corresponding amides is another important reaction in organic synthesis. This is because of the facts that the amides are versatile synthetic intermediates used in the production of pharmacological products, polymers, detergents, lubricants and drug stabilizers.[18] Conventional catalytic systems employed for this reaction require hazardous organic solvents in the presence of homogeneous strong acid and base catalysts.[19-21] However, major drawbacks of these classical methods are: i) requirement of harsh reaction conditions, which could be harmful for the sensitive functional groups, and ii) difficult to stop the reactions at the amide stage and further hydrolysis to the carboxylic acid often takes place, especially in basic media. In contrast to these catalytic processes performed in organic solvents, and despite the growing interest to develop environmentally benign and safety processes, metal catalysts able to promote such a transformation in pure aqueous media are much scarcer because of its low cost, availability, and nontoxic nature.[22,23]

Melamine and 1,4-piparazinedicarbaldehyde have been chosen for this Schiff-base condensation reaction, which could lead to the incorporation of piparazine units on edges and melamine at vertices (Scheme 1) and thus this synthesis approach results in an uniform arrangement of both nitrogen-rich components in the network. Nitrogen-rich porous organic polymeric framework could offer a large number of metal binding sites and improved thermal stability as the porous covalent imine network (CIN-1) material synthesized through the Schiff-base condensation reaction of a rigid triamine and relatively flexible dialdehyde has been found to bind active Pd sites strongly at its surface.[24] Inspired by the above observations herein, we have grafted Ag-nanoparticles at the surface of the microporous network of CIN-1 and subsequently explored its high catalytic performance in the hydration of nitriles to amide and A^3 coupling reaction by using water as the reaction medium.

Experimental section

Materials and reagents

Melamine and 1,4-piparazine dicarbaldehyde were purchased from Sigma-Aldrich. Silver nitrate ($AgNO_3$) was also purchased from Universal Chemicals, India. Sodium borohydride ($NaBH_4$) was obtained from Spectrochem, India and used as received. All other chemicals used for this investigation purposes were of analytical grade produced by Merck, India unless mentioned otherwise.

Preparation of the catalyst

Synthesis of covalent imine network materials (CIN-1)

The covalent imine network materials (CIN-1) was prepared according to the literature method.[24] A 50 ml round-bottom flask fitted with a condenser and a magnetic bar was charged with piparazine dicarbaldehyde (1.1 mmol) and melamine (0.79 mmol) and dimethyl sulfoxide (10 mL). The flask was degassed by dry nitrogen and refluxed at 180 ^{0}C for 72 h in the inert atmosphere. After cooling to room temperature the precipitated off-white product was isolated by filtration over a Buchner funnel and washed with dry ethanol and excess dry acetone, THF and dichloromethane sequentially to remove dimethyl sulfoxide completely from the porous framework. Finally, the product was dried in vacuum to obtain the desired solvent-free powder.

Synthesis of Colloidal Ag Nanoparticles

In a typical synthesis, 0.1 ml of an aqueous solution of 1% $AgNO_3$ was added to 10 ml of water containing 0.5 mm TRIS and was stirred for 2 min. Then, 0.25 ml of an aqueous solution of $NaBH_4$ (0.08%) was added drop-wise under stirring. The stirring was continued for another 10 min, and the resulting nanocolloid was stored at 4°C.

Synthesis of Ag-CIN-1 nanocatalyst *in situ*

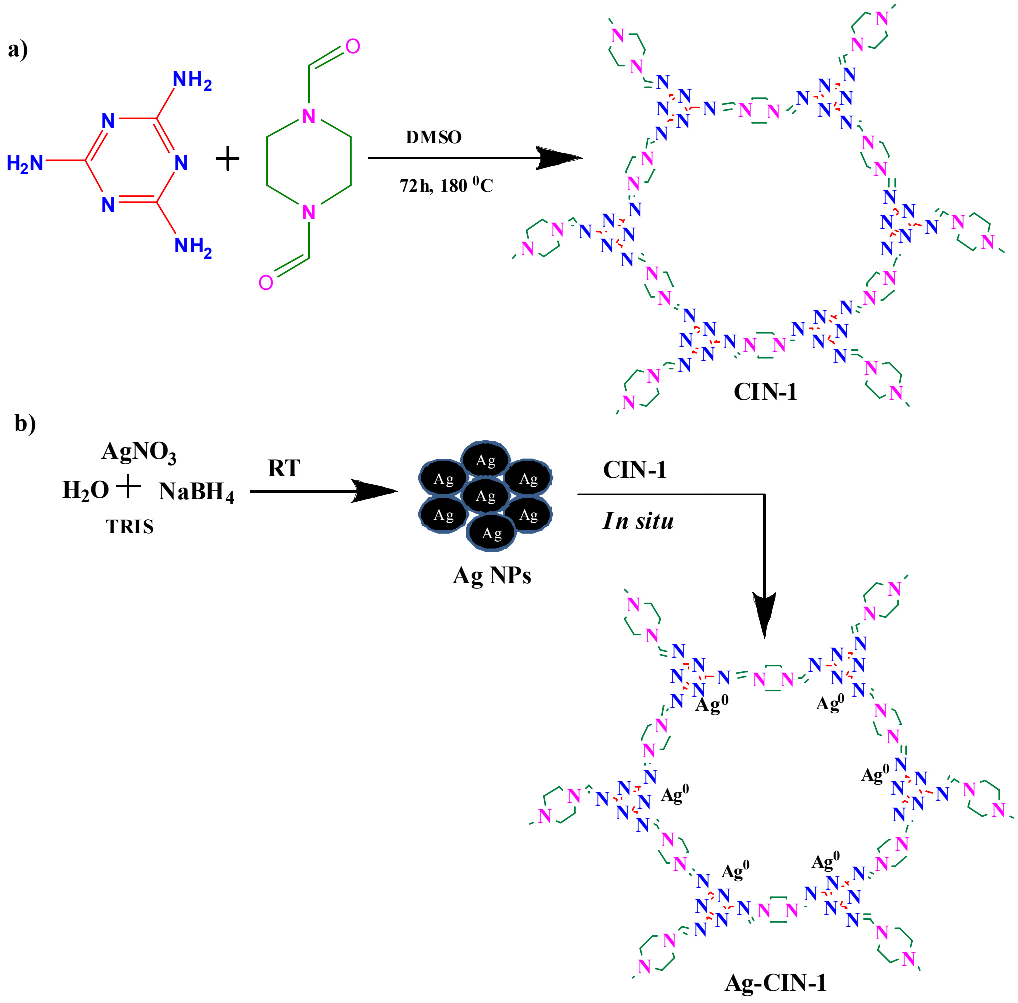
A total of 50 mg of CIN-1 was dispersed in 10 ml of TRIS-stabilized Ag-NPs and stirred for 1h at room temperature. The colour of the colloidal nanoparticles gradually disappeared while stirring. The supernatant solution was colourless after 1h of stirring at room temperature, whereas the colour of CIN-1 changed to black, indicating the loading of Ag-NPs onto the surface of CIN-1. After centrifugation, black coloured Ag-NP containing microporous polymer Ag-CIN-1 was obtained. This microporous polymer material was washed further with copious amounts of water and dried at room temperature. The loading of Ag-NPs onto CIN-1 was further confirmed by spectral measurements.

One-pot synthesis of propargylamines catalyzed by Ag-CIN-1 nanocatalyst

In a 50 mL RB flask, benzaldehyde (1.0 mmol), phenyl acetylene (1.5 mmol), piperidine (1.2 mmol), Ag-CIN-1 catalyst (0.05 g) and water (5 mL) was added. The mixture was stirred at 40 ^{0}C for 12 h. The reaction mixtures were collected at different time intervals and identified by GC-MS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 x 20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Hydration of nitriles using Ag-CIN-1 nanocatalyst

In an oven dried 50 mL RB flask Ag-CIN-1 catalyst (0.05 g), water (5.0 mL), and the corresponding nitrile (1 mmol) were stirred at 100 ^{0}C for 3h. The reaction mixtures were collected at different time interval and identified by GC-MS and quantified by GC analysis. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 x 20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 under high vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to obtain the desired product.



Scheme 1. Schematic diagram of the Ag nanoparticles grafted porous covalent imine network (Ag-CIN-1).

Characterization techniques

Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. Transmission electron microscopy (TEM) images of the mesoporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an Omicron nanotech operated at 15 kV and 20 mA with a monochromatic Al K_α X–ray source.

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. The EPR (electron paramagnetic resonance) spectra of the silver catalyst were recorded for the solid sample at room temperature by a JES-FA200 ESR spectrometer (JEOL). The reaction products were quantified (GC data) by Varian 3400 gas chromatograph equipped with a 30m CP-SIL8CB capillary column and a flame ionization detector and identified by Trace DSQ II GC-MS equipped with a 60m TR-50MS capillary column.

Results and discussion

The imine-functionalized nitrogen-rich Ag-CIN-1 has been synthesized by Schiff base condensation reaction of rigid triamine and relatively flexible dialdehyde followed by grafting with Ag NPs at its surface through impregnation (Scheme 1). Ag-CIN-1 material was thoroughly characterized by powder XRD, electron microscopy, elemental microanalysis, EPR, thermal analysis together with UV-vis spectroscopic studies.

X-ray diffraction

Figure 1A and 1B shows wide angle powder XRD pattern of CIN-1 and Ag-CIN-1 material respectively. Figure 1B shows three characteristic Bragg diffraction peaks for the silver nanoparticles with 2θ value of 38.02, 44.12, 64.29 degrees, which correspond to the face-centered cubic (fcc) phase of the silver (111), (200), (220) respectively.[25] This result suggests that in Ag-CIN-1 the Ag nanoparticles are embedded in the covalent imine network of CIN-1.

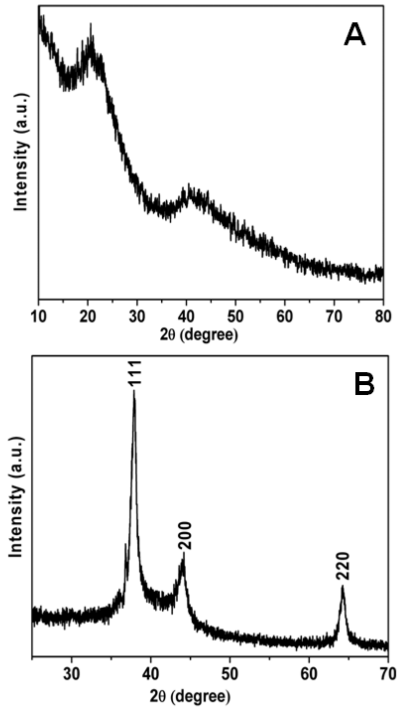


Figure 1. Wide angle powder XRD pattern of CIN-1 (A) and Ag-CIN-1 material (B).

Electron paramagnetic resonance study

A typical EPR spectrum of Ag-CIN-1 recorded at 298 K in solid state is shown in Figure 2. It shows axially symmetric signal. The g value for the corresponding signal is 1.99, which could be attributed to the presence of Ag-nanoparticles[26] in zero oxidation state, embedded into covalent imine network.[24]

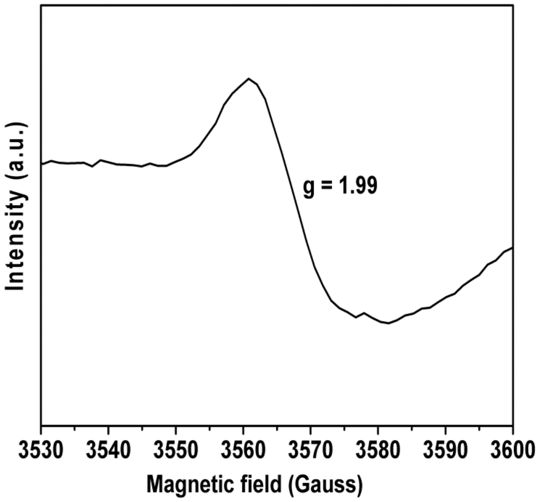


Figure 2. EPR spectrum of Ag-CIN-1

Electron microscopic analysis

In Figure 3, HR-TEM images of Ag-CIN-1 material at different magnifications are shown. It shows the presence of spherical spots of dimension *ca.*15-40 nm throughout the specimen, which could be assigned to Ag-nanoparticles in Ag-CIN-1. The FFT diffractogram of a selected area of the grid is shown in the inset of the Figure 3C. Diffraction spots in this FFT pattern suggested crystalline feature of the Ag-nanoparticles bound into the covalent imine network.

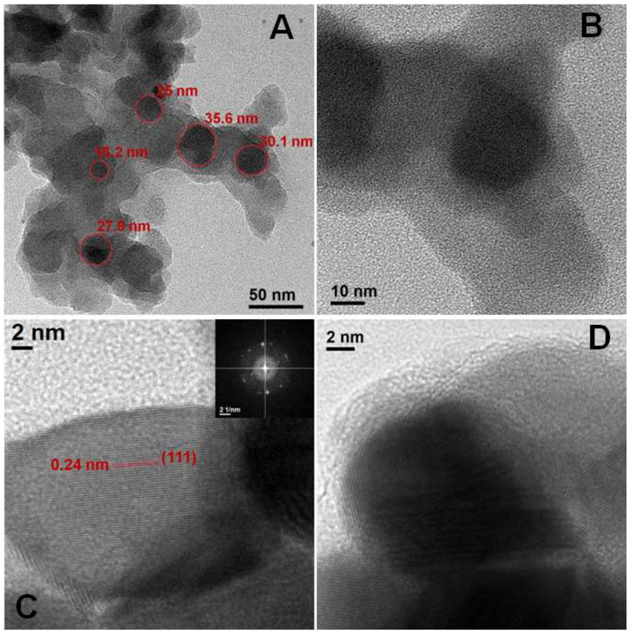


Figure 3. HR-TEM images of the Ag-CIN-1 material

XPS analysis:

In Figure 4 X-ray photoelectron spectroscopic profile of Ag-CIN-1 material is shown. The observed Ag binding energies for $3d_{5/2}$ and $3d_{3/2}$ are at 367.26 eV and 373.22 eV, respectively. These binding energy values correspond to Ag (0) nanoparticles anchored with nitrogen sites in the polymer network since the reported binding energyof Ag^0 ($3d_{5/2}$) is 368.3 eV.[27] Little shift in binding energy suggests stronger binding of Ag^0 sites with the N-sites of the covalent imine framework.

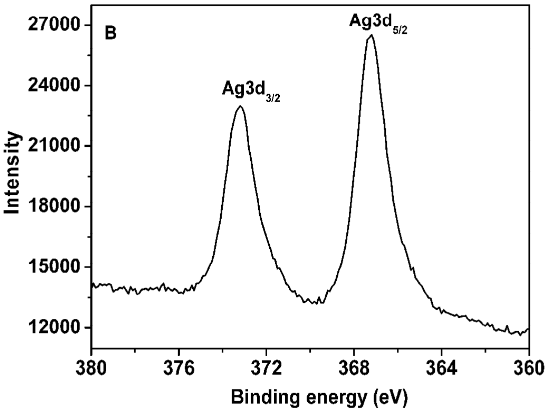


Figure 4. XPS spectrum of Ag-CIN-1.

Thermal analysis:

The quantitative determination of the organic content and the framework stability of the Ag-CIN-1 samples are obtained from the thermogravimetric (TG) and differential thermal analysis (DTA) under N_2 flow. TGA-DTA curve of Ag-CIN-1 materials are shown in Figure S1. The TGA of this material showed the first weight loss below 100 ^{0}C due to desorption of physisorbed water. This was followed by a gradual decrease in the weight after 250 ^{0}C. Thus this thermal analysis data suggested that Ag-CIN-1 microporous material is stable *ca.* 250 ^{0}C.

UV-vis spectroscopy study

In Figure 5, UV−vis spectrum of the as-prepared Ag-CIN-1 is shown. The silver nanoparticle thus formed showed an absorption peak at 370 nm corresponding to the surface plasmon resonance (SPR) of Ag NPs, suggesting the presence of Ag NPs on the CIN-1 surface.[28]

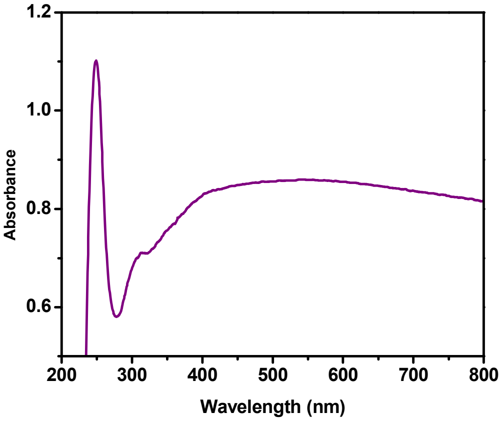
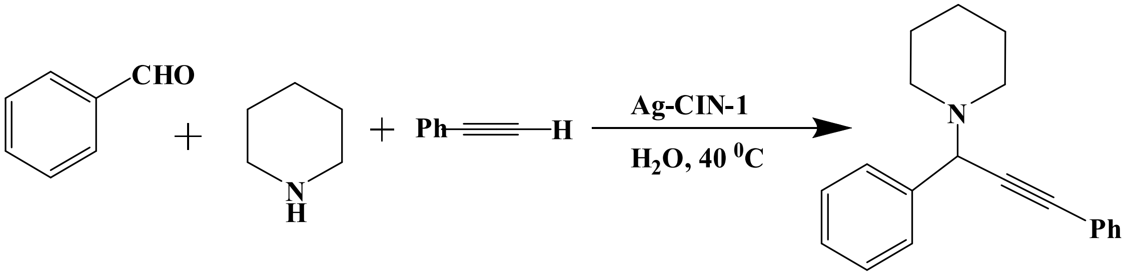


Figure 5. UV-Visible absorbance of Ag-CIN-1 material

Catalytic activity of Ag-CIN-1 for 'one-pot' A^3 coupling reactions

The catalytic activity of Ag-CIN-1 for the A^3-coupling reaction was investigated using benzaldehyde, phenylacetylene and piperidine as a model reaction using water as reaction medium at 40 ^{0}C (Scheme 2).



Scheme 2. Three-component synthesis of propargylamines catalyzed Ag-CIN-1 nanocatalyst

It has been observed that solvents play crucial role on the reactivity of the A^3 coupling reactions.[29] Our interest was to replace organic solvents by water in this reaction because it offers green chemical route. Although in toluene, DCM, THF and DMF, the catalyst system afforded the corresponding coupling product in moderate yields (Table 1, entries 2-5), MeOH, acetone and chloroform were proven to be poor solvents for the same process (entries

6–8). The reaction did not occur under catalyst-free conditions and also in the presence of metal-free CIN-1 material (entry 9 and 10) or when the reaction was carried out under room temperature (25 ^{0}C) (entry 11). From the above discussions, it can be seen that the best yield of the A^3 coupling reaction was observed when water was used as solvent at 40 ^{0}C.

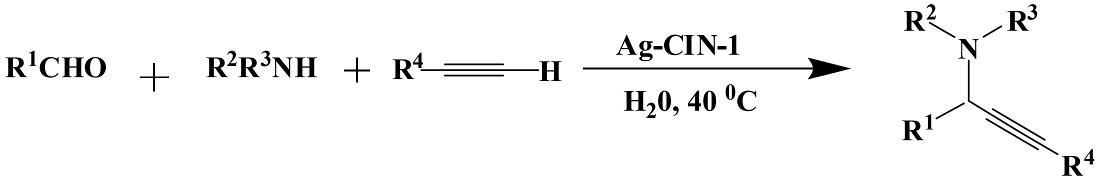
Table 1. The effects of various variables in the three-component coupling reaction (A^3 coupling) catalyzed by the Ag-CIN-1.[a]

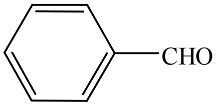
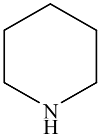
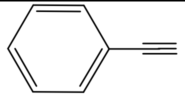
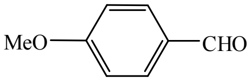
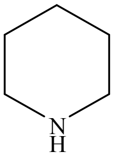
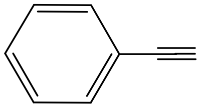
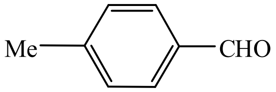
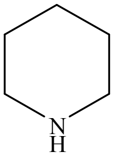
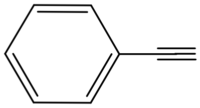
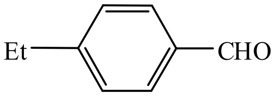
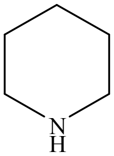
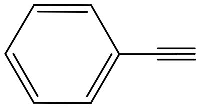
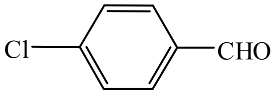
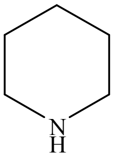
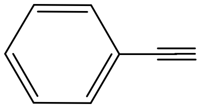
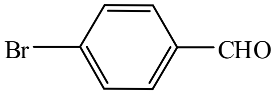
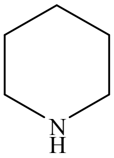
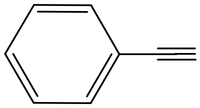
Entry	Solvent	Temperature (^{0}C)	Yield (%)[b]
1	**H_2O**	**40**	**98**
2	DMF	40	45
3	THF	40	62
4	DCM	40	70
5	Toluene	40	76
6	MeOH	40	10
7	Aectone	40	32
8	chloroform	40	36
9[c]	H_2O	40	Trace
10[d]	H_2O	40	Trace
11	H_2O	RT (25 ^{0}C)	Trace

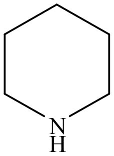
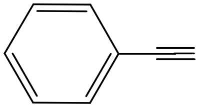
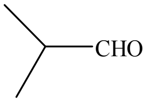
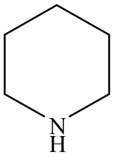
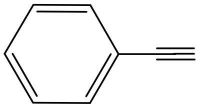
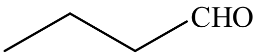
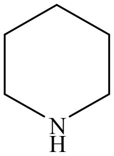
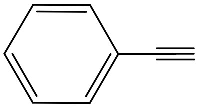
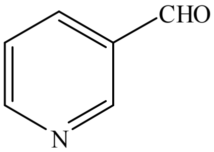
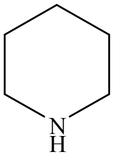
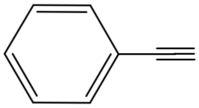
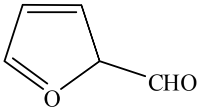
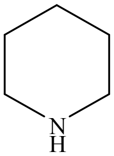
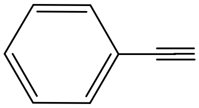
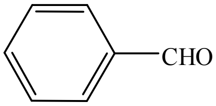
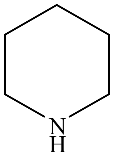
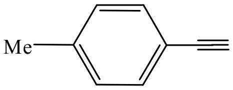
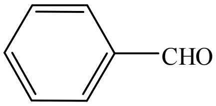
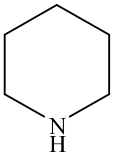
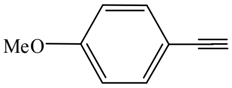
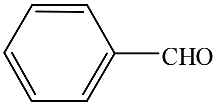
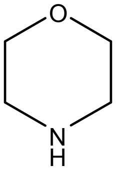
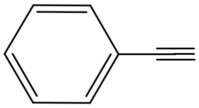
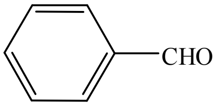
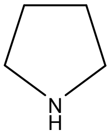
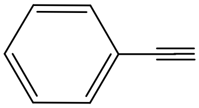
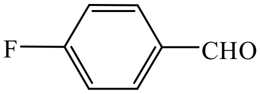
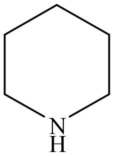
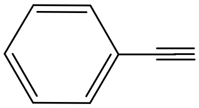
[a] **Reaction conditions :** benzaldehyde (1.0 mmol), phenyl acetylene (1.5 mmol), piperidine (1.2 mmol), Ag-CIN-1 catalyst (0.05g) and solvent (5 ml). [b] Yield determined by GC and GCMS analysis. [c] metal free CIN-1 ligand and [d] without catalyst

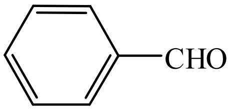
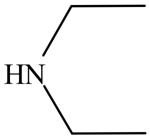
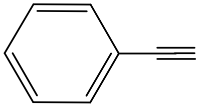
To expand the scope of this A^3-coupling, various aldehydes, alkynes and amines were used as substrates under the optimized reaction conditions. The results are summarized in Table 2. From the table 2 it is clear that the conditions were equally applicable to the coupling of a variety of aromatic and aliphatic aldehydes including heterocyclic aldehydes with various amines utilizing phenylacetylene, giving the corresponding propargylamines in high yields at 40 °C.

Table 2. The three-component (A^3) coupling reaction catalyzed by the Ag-CIN-1 nanocatalyst.[a]



Entry	Aldehyde	Amine	Alkyne	Yield (%)[b]
1				98
2				87
3				91
4				81
5				74
6				79

7	HCHO			74
8				78
9				81
10				81
11				85
12				91
13				86
14				65
15				73
16				65

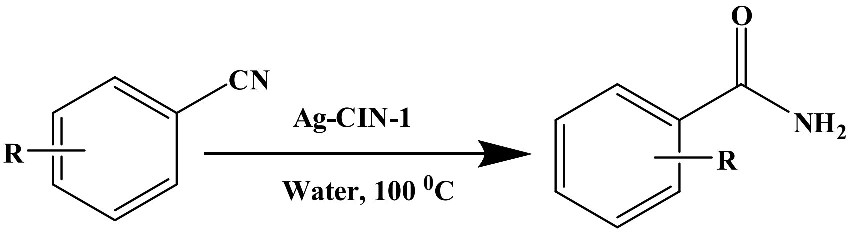
17				31

^{a}Reaction conditions: aldehyde (1.0 mmol), alkyne (1.5 mmol), Amine (1.2 mmol), Ag-CIN-1 catalyst (0.05g) and water (5 ml), ^{b}Yield determined by GC and GCMS analysis. Products were identified by comparison of their ^{1}H-NMR spectral data those reported in the literature.

Both aromatic and aliphatic aldehydes, including those bearing functional groups such as alkoxy, chloro and bromo additions, were able to undergo the corresponding three-component-coupling. Irrespective of the electronic nature of the substituent, aromatic aldehydes reacted smoothly to give the corresponding products in good yields (entries 2-6). On the other hand, aliphatic aldehydes (entries 7–9) reacted rapidly and gave excellent yields without any trimerization. Aryl aldehyde possessing an electron-withdrawing group afforded slightly lower yield than the electron-donating group. It is worth noting that 4-flurobenzaldehyde gave lower yield of the coupled product despite long reaction times (entry 16). In addition, heteroaromatic aldehydes displayed high reactivity and gave good yields of products (entries 10–11). We also found that a variety of terminal aromatic alkynes with substituted groups in *para* -positions could be effectively reacted under the present reaction conditions (Table 2, entries 12-13). Note that the reactions proceeded smoothly to give the corresponding propargylamines in a good yield. Good yields were observed when cyclic dialkylamines such as pyrrolidine and morpholine and also aromatic amine were used (entries 14 and 15), whereas the diethylamine afforded a lower conversion (entry17).

The catalytic hydration of nitrile using Ag-CIN-1 nanocatalyst

The hydration of nitriles is one of the most imperative technologies for the large-scale synthesis of amides, which are a very significant group of compounds in the chemical and pharmaceutical industry. The catalytic activity of microporous Ag-CIN-1 was tested for the hydration of benzonitrile under aqueous conditions without organic solvents. Here, we have explored the catalytic efficiency of the Ag-CIN-1 nanocatalyst in hydration of nitriles in green solvent water at 100 °C (Scheme 3).



Scheme 3. Ag-CIN-1-catalyzed hydration of benzonitrile to benzamide in water

For hydration of nitriles over Ag-CIN-1, the reaction parameters are optimized using benzonitrile as a model substrate and the results are summarized in Table 3. Without any catalyst and catalyst alone without any solvent (Table 3, entries 10 and 11) no reaction occurred at 100 °C. Among the different solvents employed to optimize the reaction conditions, only water has shown highest catalytic activity (Table 3).

Table 3. Optimization of reaction conditions in synthesis of benzamide from benzonitrile catalyzed by Ag-CIN-1 nanocatalyst[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	Toluene	5	--
2	Acetonitrile	5	trace
3	Dichloromethane	5	--
4	THF	5	trace

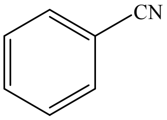
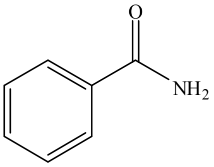
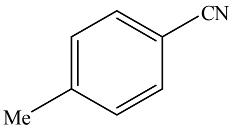
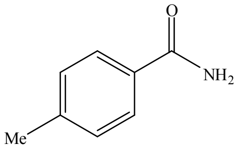
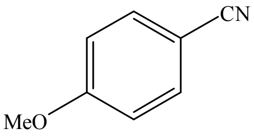
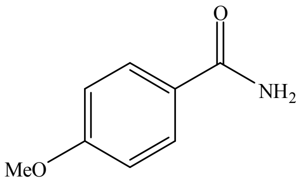
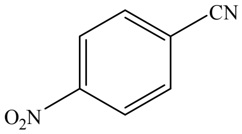
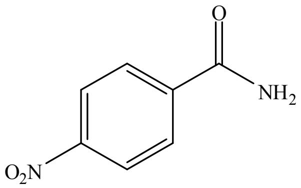
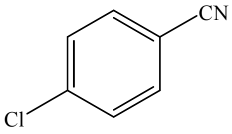
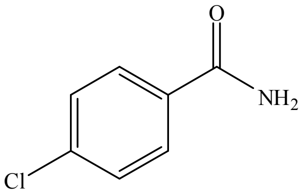
5	Ethanol	3	20
6	Methanol	3	24
7	Methanol/water (1:2)	3	72
8	Methanol/water (1:1)	3	51
9	**Water**	**3**	**96**
10[c]	water	3	No Reaction
11	--	3	No Reaction

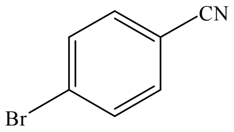
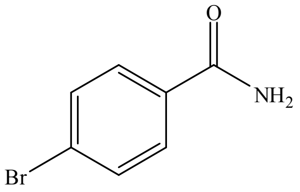
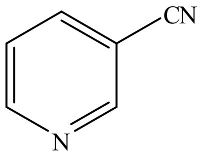
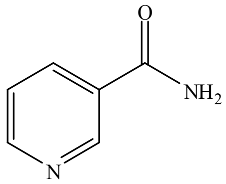
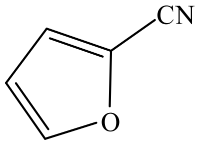
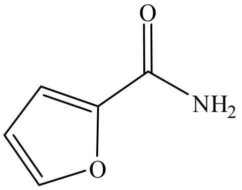
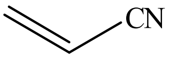
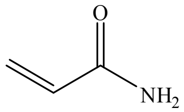
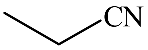
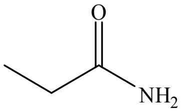
[a]Reaction Condition: Ag-CIN-1 catalyst (0.05g), solvent (5.0 ml), benzonitrile (1 mmol); [b]Yield determined by GC and GCMS analysis and [c] Without catalyst.

Under the optimized reaction conditions, the protocol is also extended to various nitriles. The scope of the present Ag-CIN-1 nanocatalyst system with regard to various kinds of nitriles was examined. The results are summarized in Table 4. A large numbers of aromatic nitriles (entries 1–8) as well as an aliphatic nitrile (entries 9-10) are smoothly hydrated to the corresponding amide in excellent yield. Aromatic nitriles carrying either electron-donating such as *p*-methyl and *p*-methoxy or electron-withdrawing such as *p*-bromo, chloro and *p*-nitro groups exhibit comparable reactivity and react efficiently to yield the final product (entries 2-6). Usually, the hydration of heteroaromatic nitriles is more difficult and the reaction rates are much lower than those of common nitriles because of their strong coordination to the metal centers. In the present study, hydration of 3-cyanopyridine (78%) and also furan-2-carbonitrile (83%) afforded the corresponding amides in near quantitative yields (entries 7-8).

The less reactive aliphatic nitriles could also be hydrated to the corresponding aliphatic amides (entries 13 and 14).

Table 4. Hydration of various nitriles catalyzed by Ag-CIN-1 nanocatalyst[a]

Entry	Nitrile	Amide	Yield (%)[b]
1			96
2			82
3			86
4			78
5			74

6			82
7			78
8			83
9			63
10			73

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[a]Reaction Condition: Ag-CIN-1catalyst (0.05g), water (5.0 ml), nitrile (1 mmol) temperature (100 ^{0}C); [b]Yield determined by GC and GCMS analysis.

Recycling efficiency of the catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of Ag-CIN-1 nanocatalyst was investigated in ‘one-pot’ A^3-coupling reactions and hydration of various nitriles under the optimized reaction conditions. After each run, ethyl acetate was added to dilute the reaction mixture and the organic layer was dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified. After a simple wash using ethyl acetate and dried, the catalyst was reused for the next run and almost consistent activity was observed for next five consecutive cycles. As seen from Fig. 6, the recycled catalyst did not show any appreciable change in the activity which indicates that the catalyst is stable and can be regenerated for repeated use.

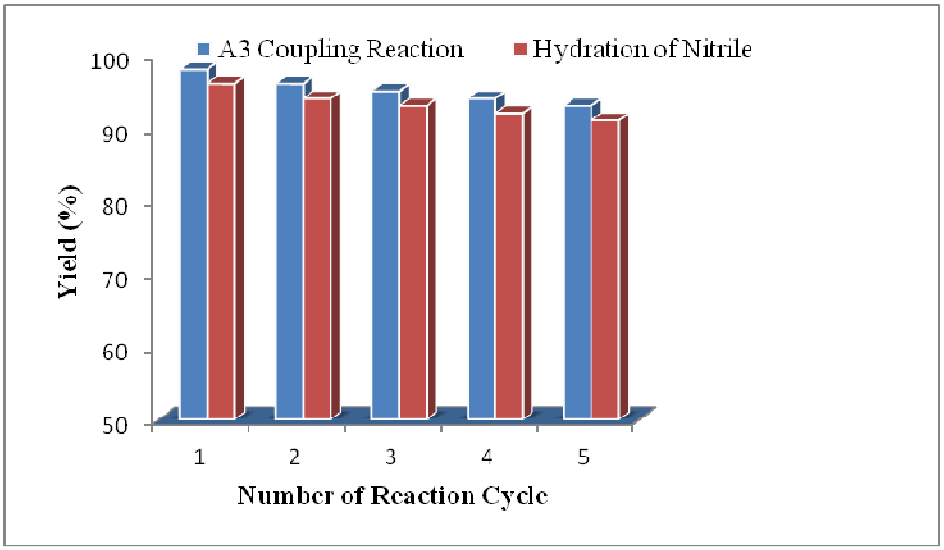

Figure 6. Recycle efficiency of Ag-CIN-1 nanocatalyst for A^3-coupling reaction and hydration of nitrile

Characterization of reused catalyst

The reused catalyst have been characterized by employing wide angle powder XRD, TEM and EPR studies to clarify if any change occur in the catalyst after catalysis. In the wide angle powder XRD pattern of the reused catalyst (Fig.S2) three characteristic Bragg diffraction peaks for the Ag nanoparticles are observed, which suggest that the face-centered cubic (fcc) phase of the silver are well preserved during the course of the catalytic reaction. The TEM images of the reused Ag-CIN-1 after the fourth catalytic cycle (Fig.S3) show that

Ag nanoparticles are well embedded in CIN-1 polymer after the reaction. We have taken the EPR spectra of the reused catalyst after the fourth catalytic reaction cycle at 77 K temperature in solid state (Fig.S4). It also shows axially symmetric signal with g value 1.97. The above results reveal that Ag-CIN-1 catalyst is very stable during the catalysis.

Heterogeneity Test

To examine whether silver was being leached out from the solid support to the solution, experiment has been carried out in the one- pot three-component coupling reaction with our supported Ag-CIN nanocatalyst. A typical filtration test was performed in the one-pot three-component coupling reaction of benzaldehyde, phenyl acetylene and piperidine (A^3-coupling) to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture after 4 h and the filtrate was allowed to react up to the completion of the reaction (6 h). In this case no change in conversion was observed, which suggests that the catalyst is heterogeneous in nature. No evidence for leaching of silver or decomposition of the complex catalyst was observed during the catalytic reaction. It was noticed that after filtration of the catalyst from the reactor at the reaction temperature, coupling reactions do not proceed further. Atomic absorption spectrometric analysis of the supernatant solution of the reaction mixture thus collected through filtration also confirmed the absence of silver ions in the liquid phase. Thus, results of the hot filtration test suggested that silver was not being leached out from the solid porous polymer catalyst during the cross-coupling reactions.

Comparison with other reported systems

Synthesis of propargylamines and hydration of nitriles over a variety of heterogeneous catalysts have been summarized in Table 5. It provides a comparative catalytic activity of Ag-CIN-1 over related catalytic systems reported in the literature.[30-35] From Table 5, it is seen that present catalyst exhibited higher yields compared to the other reported system.

Table 5. Comparison of catalytic activity of the present catalyst in Synthesis of propargylamines and Hydration of Nitriles with other reported systems

Entry	Catalyst	Reaction Conditions	Yield (%)	Ref.
1	nanoferrite–$[Ru(OH)]_x$	water, 130 ^{0}C, 30 min,	85	29
2	Ni NPs/HT	water, 120 °C,10h	85	30
3	AgHAP	water, 140 ^{0}C. 3h	94	31
4	Ag-CIN-1 nanocatalyst	water, 100 ^{0}C, 3h	96	This study
5	NHC silver complexes	Dioxane, 100 ^{0}C, 12 h	81	32
6	Polymer-supported NHC–Ag(I)	CH_2Cl_2, RT, 24 h	92	33
7	Au@PMO-IL	$CHCl_3$, 60 ^{0}C, 11 h	87	34
8	Ag-CIN nanocatalyst	water, 40 ^{0}C,12h	98	This study

Conclusions

From the above results we can conclude that a facile synthesis of silver grafted imine-functionalized nitrogen-rich porous organic network (Ag-CIN-1) can be developed from the precursor organic monomer building blocks through an easy chemical route and the resulting material showed excellent catalytic activity towards ‘one-pot’ A^3-coupling reactions and hydration of various nitriles in green solvent. The high amount of nitrogen in the CIN-1 support makes the silver nanoparticles resistant to aggregation and also helps to preserve their catalytic activity and stability during recycling. Thus the catalytic process is green and environmental friendliness and it offers a number of advantages, such as excellent stability, easy separation from the reaction mixture by filtration, reusability for several times with often minimal loss of activity. Thus, these key findings reported herein based recyclable heterogeneous catalysis would open-up advanced, economical and environmentally sustainable routes for the synthesis of propargylamines and hydration of various nitriles.

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