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Aerobic Oxidative Synthesis of Aryl Nitriles and Primary Aryl Amides from Benzylic Alcohols Catalyzed by Polymer Supported Cu(II) Complex

Rostam Ali Molla,[a] Kajari Ghosh,[a] K. Tuhina,[b]* S. M. Islam,[a,]*

[a]*Department of Chemistry,University of Kalyani, Kalyani, Nadia 741235, W.B., India.*

[b]*Department of Chemistry, B.S. College, Canning, S-24 PGS, 743329, W.B., India.*

Abstract

A new polymer supported Cu (II) complex has been synthesized and characterized. The catalytic performance of the complex has been tested for the direct conversion of benzylic alcohols to aryl nitriles. In this reaction ammonium formate was used as the nitrogen source and O_2 as the oxidant. Furthermore, copper-catalyzed one-pot synthesis of primary aryl amides from alcohols was also achieved. The effects of solvents, reaction time and catalyst amount for the aryl nitriles and aryl amides synthesis were reported. This catalyst showed excellent catalytic activity and recyclability. The polymer supported Cu (II) catalyst could be easily recovered by filtration and reused more than five times without appreciable loss of its initial activity.

Key words: Polymer supported catalyst, copper, benzylic alcohols, aryl nitriles, primary aryl amides.

* *Author to whom correspondence should be addressed. Dr. Sk. Manirul Islam*, [a]*Department of Chemistry, University of Kalyani ,Kalyani, Nadia, 741235, W.B., India Phone: + 91- 33-2582-8750, Fax: 91-33-2582-8282, E-mail: manir65@rediffmail.com*

K. Tuhina, [b]*Department of Chemistry, B.S. College, Canning, S-24 PGS, 743329, W.B., India. Email: tuhina31@yahoo.com*

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Introduction

Selective oxidation of organic compounds by a catalytic method using O_2 or air as an oxidant has become urgent from the viewpoints of green chemistry.[1-5] Aryl nitriles are versatile building blocks in the synthesis of natural products, pharmaceuticals, agricultural chemicals and dyes.[6-9] Therefore, the development of an efficient catalytic system has recently been investigated for the synthesis of aryl nitriles. Initially, it was prepared by the nucleophilic substitution of halides with cyanide ions, However, inorganic cyanide salts, generally toxic, were used and the reactions produce large amounts of inorganic salts as waste. Environmentally benign approaches are considerably attractive, and many excellent examples have been reported. For instance, metal-catalyzed dehydration of aryl oximes or amides, changing the CN source to DMF *via* the C-H functionalization of arenes, and especially, oxidative dehydrogenation of benzylic alcohols, azides or methyl arenes have been extensively investigated.[10-27]

On the other hand, primary amides are also an important class of compounds that are used as starting materials for engineering plastics, detergents, and lubricants.[28] In organic synthesis, primary amides are potent substrates for primary amines, nitriles, amino acid derivates, and heterocycles preparation.[29] Biologically, primary amides are present in numerous biologically active molecules.[30] Based on their importance, several methodologies have been developed for their synthesis.[31]

With regard to synthesis of primary amides, hydration of nitriles[32,33] and rearrangement of aldoximes[34] are attractive procedures. Currently, benzonitrile, its derivatives and acrylonitrile are being industrially produced by ammoxidation. Thus, for synthesis of benzamide derivatives and acrylamide, hydration is a reliable procedure from both environmental and economical viewpoints. In contrast, other nitriles have generally been synthesized by costful non-green

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procedures[35] and hydration is not the best choice in these cases. Although the atom efficiency of rearrangement of aldoximes itself is theoretically 100%, the formation of hydrochloric acid or sulfuric acid is typically inevitable for preparation of aldoximes.

As alcohols are easily available and inexpensive, it would be advantageous to synthesize nitriles and primary amides directly from alcohols. Catalytic synthesis of aryl nitrile from alcohol has been reported[36]. Amidation of alcohols with ammonium formate as the nitrogen source is an attractive reaction. Until now, only a few systems for amidation of alcohols or aldehyde have been reported where ammonia was used as the nitrogen source.[37] But these methods suffer from several drawbacks because most of them are used homogeneous catalytic system. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse. Recently, some heterogeneously metal catalyzed primary amide synthesis from primary alcohol has been reported.[38] In order to overcome problems related to the homogeneous catalysts, several supported systems were developed by us[39]. Aerobic oxidative synthesis of nitriles and primary amides from alcohol catalysed by heterogeneous copper catalysts are still rare. To get rid from these serious issues, it is thus desirable to develop an efficient methodology to avoid all these difficulties.

Thus, we have synthesized polymer supported bis(2-hydroxyanyl)acetylacetonato copper (II) Schiff base complex (PS-BHA-Cu) as an effective and highly reusable catalyst. Here we report a green one pot procedure for the synthesis of aryl nitriles and primary aryl amides from benzylic alcohols catalyzed by PS-BHA-Cu catalyst and O_2 as the oxidant.

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Experimental Section

Materials

Analytical grade reagents and freshly distilled solvents were used throughout the experiments. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures. 5.5% crosslinked chloromethylated polystyrene and copper acetate were purchased from Sigma Aldrich and used as without further purification.

Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Perkins Elmer FT-IR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The EPR (electron paramagnetic resonance) spectra of the fresh and used PS-BHA-Cu catalyst were recorded for the solid sample at room temperature using a JES-FA200 ESR spectrometer (JEOL). Copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). NMR spectra were recorded on a Varian Mercury plus NMR spectrometer (^{1}H NMR at 300 and 500 MHz) in pure deuterated solvents.

Preparation of polymer supported bis(2- hydroxylanyl)acetylacetone (PS-BHA)

To a 20 mL DMF in a 100 mL round bottom flask 1 gm chloromethylated polystyrene, 2 gm of bis(2- hydroxylanyl)acetylacetone and 0.03 g NaI were added and heated at 110 °C for 5 days

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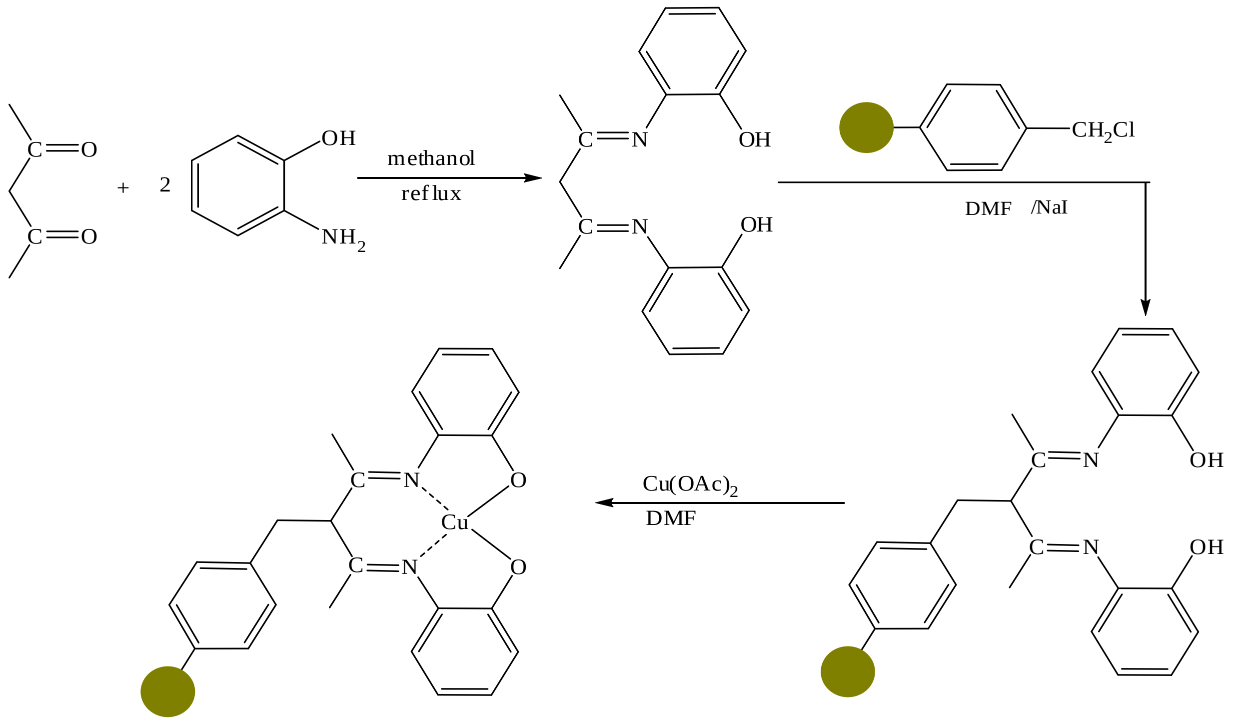
with stirring. After cooling to room temperature the mixture was filtered and washed thoroughly with methanol and dried in an oven at 80 °C.

Preparation of polymersupported bis (2- hydroxylanyl) acetylacetonato copper Schiff base catalyst (PS-BHA-Cu): To a 10 mL DMF in a 50 mL round bottom flask was added 500 mg of polymer-supported bis(2- hydroxylanyl)acetylacetone. After stirring for 1h to swell the polymer, 100 mg of $Cu(OAc)_2$ was added to this mixture and the content was heated for 3 h at 110 °C. Then the content was filtered and the beads were washed thoroughly with chloroform and dried in an oven at 80 ^{0}C.



PS-BHA-Cu (II)

PS-BHA

Scheme 1 Preparation of polymer anchored Cu(II) complex

General procedure of synthesis of aryl nitriles from benzylic alcohols

To a 50 mL round-bottomed flask equipped with a magnetic stirrer, 15 mg of (PS-BHA-Cu), 0.05 mmol K_3PO_4, 2.0 mmol $HCOONH_4$, 0.5 mmol of benzylic alcohol and 3 mL of ACN

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were added. The vessel was flushed with O_2 (1 atm). The vessel was sealed and the reaction mixture was stirred at 115 ^{0}C temperature for 16 hours. After cooling to room temperature, the mixture was partitioned between ethyl acetate and brine. The organic layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4. The residue was purified by column chromatography (silica gel, EtOAc-PE). All the prepared compounds were confirmed by ^{1}H NMR.

General procedure of synthesis of primary aryl amides from benzylic alcohols

To a 50 mL round-bottomed flask equipped with a magnetic stirrer was charged with DMF (3 mL), 0.15 mmol of (PS-BHA-Cu), 0.15 mmol of TBHP, 3.0 mmol of benzylic alcohol, 25% aq. ammonia 2.6 equiv. with respect to substrate and O_2 (1atm) before heating at 80 ^{0}C for 5h. After cooling the reactor, the O_2 was vented from the reactor and the desired compound was purified by chromatography on silica gel using silica gel, EtOAc-PE. All the prepared compounds were confirmed by ^{1}H NMR.

Results and Discussion

Characterization of the polymer supported catalyst.

Due to insolubility of the polymer supported copper catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM-EDX, TGA, IR and UV-vis spectroscopic data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported copper catalyst. Copper content in the catalyst determined by AAS suggests 4.85 wt% Cu in the catalyst. The complexation ratio of copper and Schiff base is 1:1.3.

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Table 1: Chemical composition of polymer anchored ligand and polymer supported catalyst

Compound	C%	H%	Cl %	N%	metal%
PS-BHA	85.41	7.49	1.22	3.74	-
PS-BHA-Cu	82.30	7.21	1.10	3.68	4.85

The IR spectra of the synthesized Schiff base PS-BHA showed a broad band between 2855 and 3409 cm^{-1} due to intermolecular hydrogen bonding $v_{(\text{N-H})}$ and $v_{(\text{OH})}$ enolic vibrations. The appearance of the absorption band at ≈1700 cm^{-1} was an indication of the presence of free carbonyl groups of some unreacted acetylacetone in the prepared Schiff base and complex. A strong absorption band at 1604 cm^{-1} was assigned to the (C=N) azomethine group, and the absorption band between 1061 and 1107 cm^{-1} was attributed to v(C-O) vibrations. The Schiff base showed a band at 1574 cm^{-1} that corresponded to the v(C=C) group. In complex the intensity of the absorption band corresponding to enolic OH reduced greatly, which was present in the PS-BHA between 2855 and 3409 cm^{-1}. This reduction in the absorption bands in the IR spectra of the PS-BHA-Cu provided evidence for its complexation with copper(II) ions. On complexation, two new bands at 480 and 502 cm^{-1} appeared that corresponded to vibration frequencies of bonds formed between copper(II) ions with the enolic oxygen and nitrogen atoms of the azomethine of the Schiff base.

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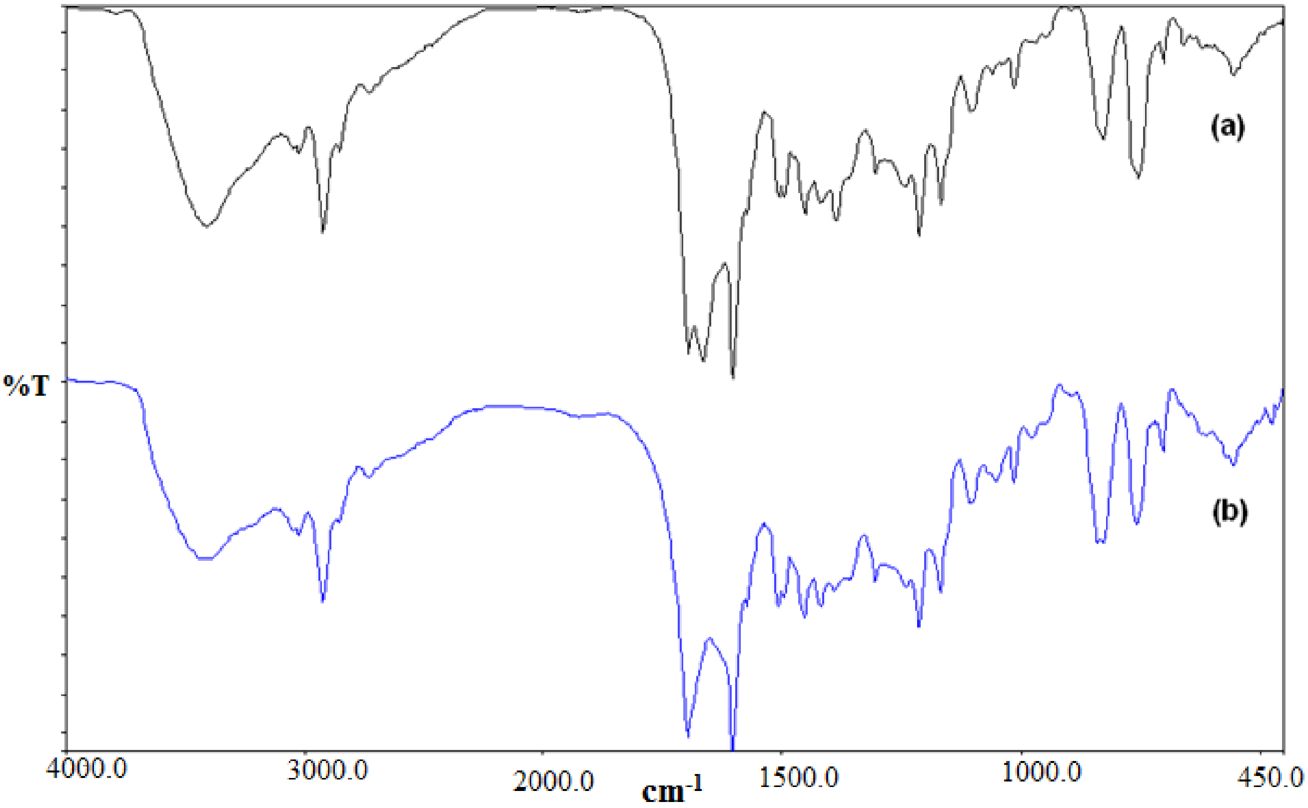

Fig.1. FT-IR Spectra of polymer anchored ligand PS-BHA (a) and PS-BHA-Cu complex (b)

The electronic spectra of the Schiff base PS-BHA showed two absorption bands at 258 and 319 nm for π-π* and *n*-π* transitions in the Schiff base. The electronic spectra of the ligand on complexation also showed variations in the absorption bands corresponding to π-π* and *n*-π* transitions. Two new absorption bands at 345 nm and 370 nm in the electronic spectrum of the copper (II) complex were attributed to LMCT. In this complex, the bands around 410-435 nm are due to d-d transition.[40]

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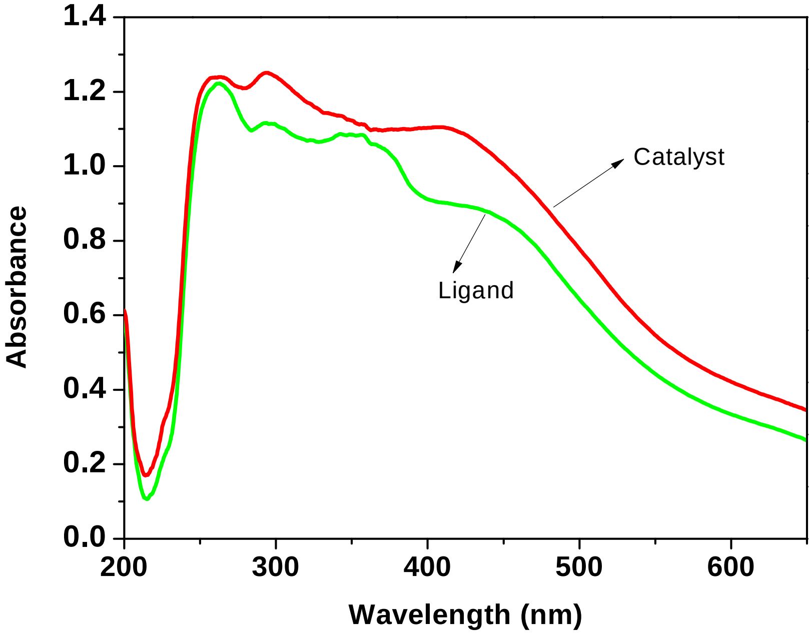

Fig.2. DRS-UV-visible absorption spectra of the polymer supported ligand(a) and catalyst(b).

The scanning electron micrographs of PS-BHA (Fig. 3a) and supported PS-BHA-Cu catalyst (Fig. 3b) clearly show the morphological change which occurred on the surface of polystyrene after loading of metal on it. An energy dispersive spectroscopy analysis of X-rays (EDX) data for PS-BHA-Cu catalyst is given in Fig. 4. The EDX data also inform that the attachment of copper metal on the surface of the polymer matrix.

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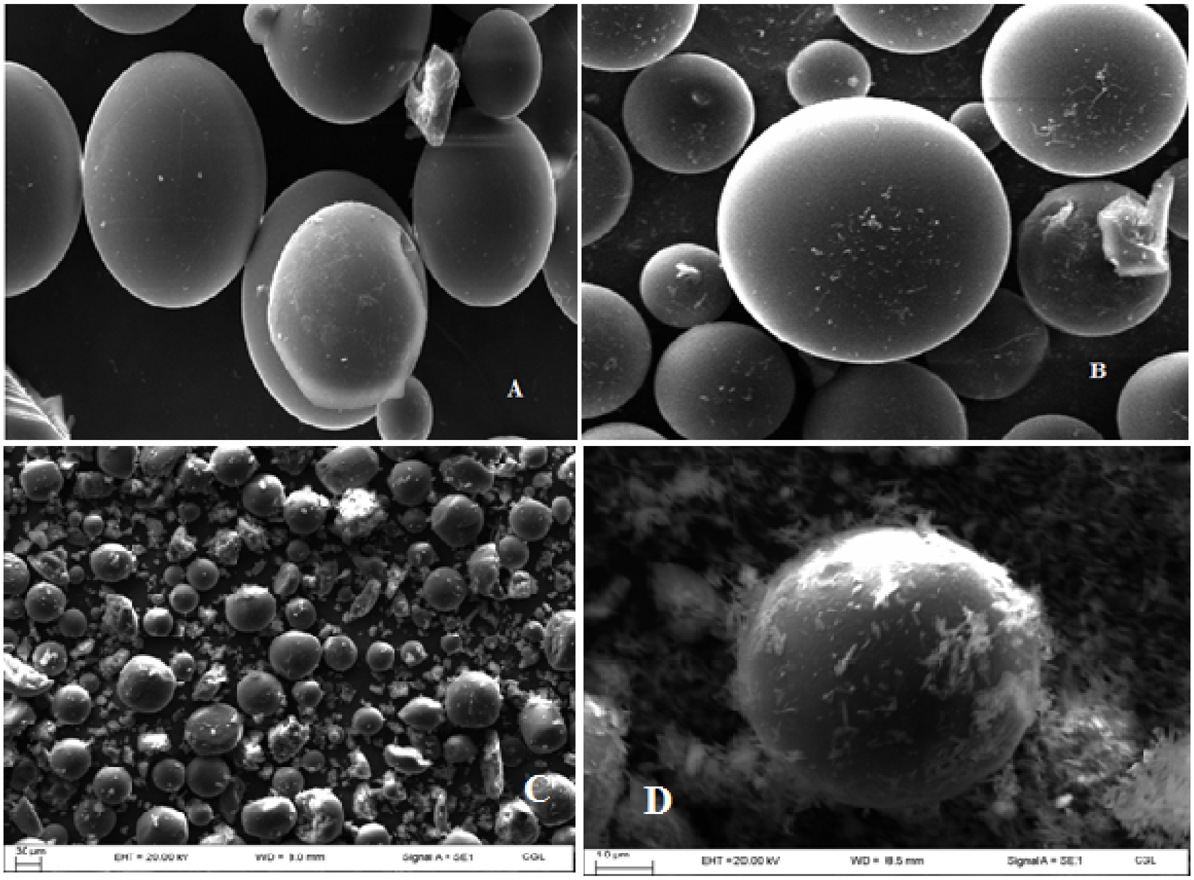

Fig.3. FE-SEM images of polymer anchored ligand PS-BHA (A, B) and PS-BHA-Cu (C,D) complex

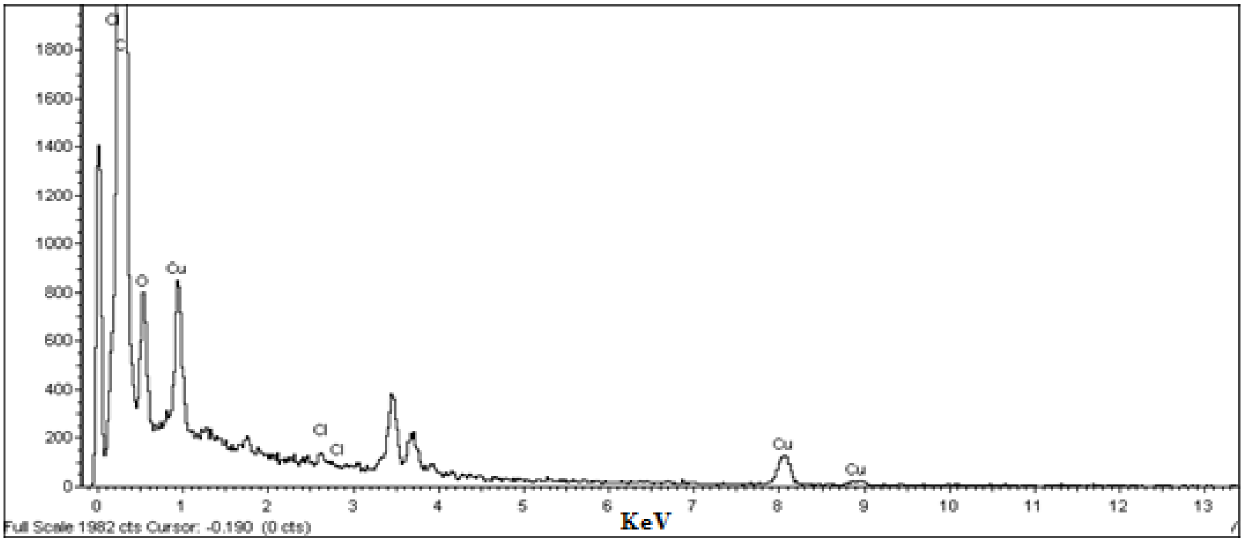

Fig.4. EDX image of polymer anchored complex PS-BHA-Cu

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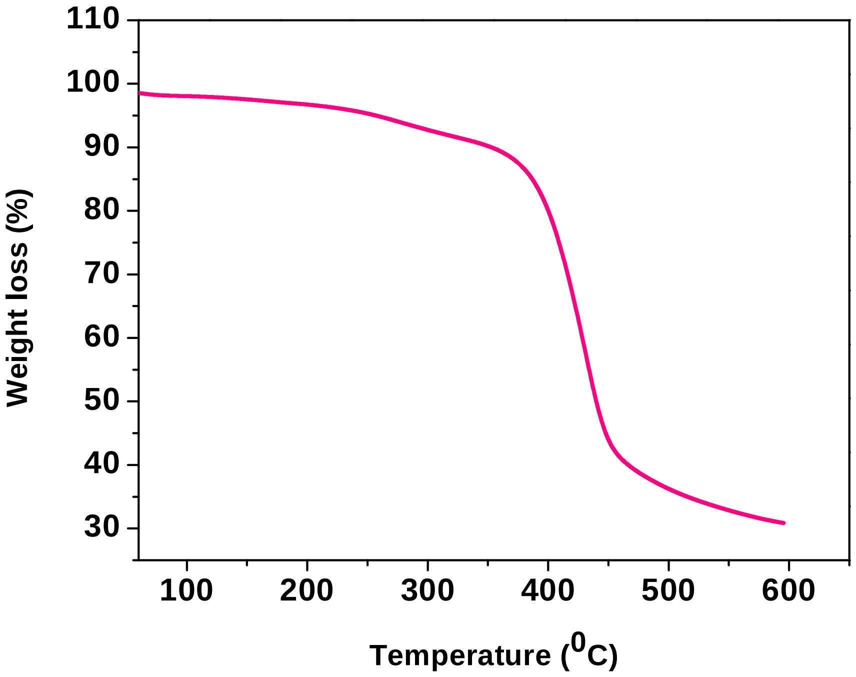

Fig. 5. Thermogravimetric weight loss plots for the polymer supported catalyst.

Thermal stability of the complex was investigated using TGA-DTA at a heating rate of 10 ^{0}C / min in air over a temperature range of 30–600 ^{0}C. TGA-DTA curve of the polymer anchored catalyst is shown in Fig. 5. The PS-BHA is stable up to 330 ^{0}C and thermal decomposition of the catalyst is start above this temperature. Finally degradation of the PS-BHA-Cu catalyst is occurred above the temperature 380 ^{0}C. So, we can suggest that the complex is stable up to 360 ^{0}C and above this temperature it starts decomposes. Thermo gravimetric study suggests that the polymer anchored catalyst degrades at considerably higher temperature.

Catalytic activities

Since polymer anchored metal systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we have decided to investigate the catalytic activity of polymer anchored Schiff base copper complex in the field of

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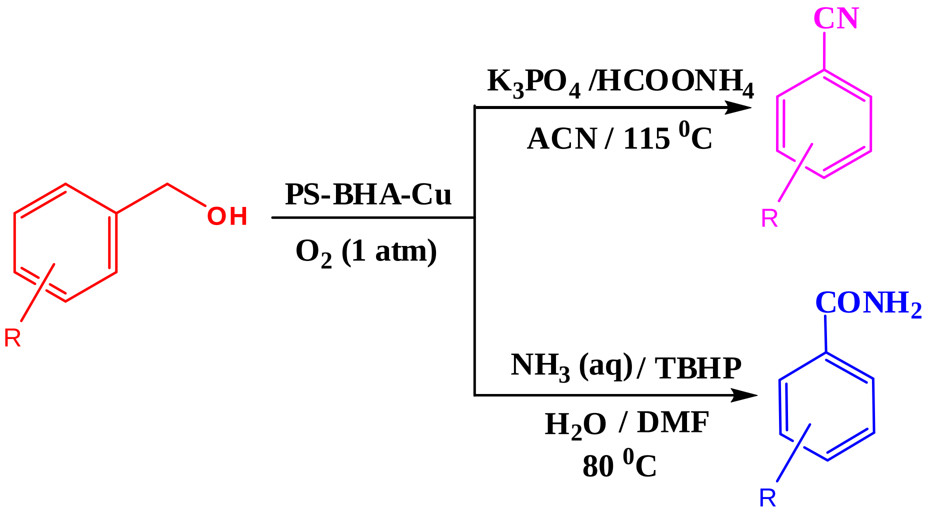
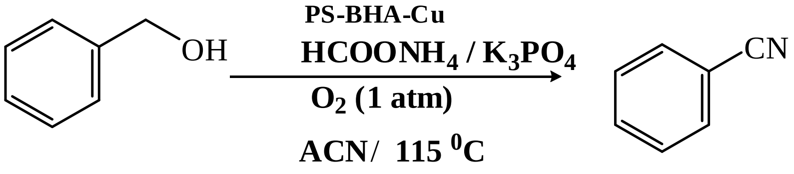
aerobic oxidative synthesis of aryl nitriles from benzylic alcohols and ammonium formate. Also we have studied the synthesis of primary aryl amides from benzylic alcohols.



Scheme 2: Aerobic oxidative synthesis of aryl nitrile and aryl amide

Aerobic oxidation of benzylic alcohols into nitriles

To test the catalytic activity of the present catalyst, first aerobic oxidation of benzylic alcohols into nitriles was tested at 115 ^{0}C for 16h. Ammonium formate was used as the nitrogen source and K_3PO_4 was used as the base. For optimization of reaction conditions, we choose the aerobic oxidation of benzyl alcohol as a probe reaction. In this case benzyl alcohol is selectively converted to benzonitrile (98 %) along with very small amount of benzaldehyde (2%) in the presence of PS-BHA-Cu and ammonium formate under reaction conditions (Scheme 3).



Scheme 3 aerobic oxidation of benzylic alcohols into nitriles.

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To find the appropriate reaction conditions various solvents were screened and in order to identify effective reaction conditions, the reaction was carried out under various catalyst amount and reaction time (Table 2). We investigated the ability of various solvents like ACN, DMF and dioxane. The conversion and selectivity of benzonitrile is highest in ACN as compared to the other solvents like DMF and dioxane. The variation of conversion of the benzyl alcohol at the given conditions showed that the conversion increased with polymer anchored Cu (II) catalyst. It has been observed that increase in initial catalyst amount from 5 mg to 20 mg enhance the conversion from 55% to 94%. Maximum conversion was found at 15 mg catalyst. Also the reaction was carried out at different time ranging from 10h to 16h and it was found that at 16h the conversion of benzyl alcohol was 94% at given conditions.

Table 2: Effect of solvent, reaction time and catalyst amount on aryl nitrile synthesis.

Entry	Solvent	Catalyst amount (mg)	Time (h)	Conversion (%)	Selectivity (%)
1	ACN	5	10	55	99
2	ACN	10	13	73	98
3	ACN	15	16	94	98
4	DMF	15	16	87	96
5	dioxane	15	16	79	96
6	ACN	20	16	94	96

Reaction conditions: alcohol (0.5 mmol), PS-BHA-Cu (15 mg), $HCOONH_4$ (2.0 mmol), K_3PO_4 (0.05 mmol), ACN (3 mL), O_2 (1 atm.), Temperature (115 ^{0}C), 16h.

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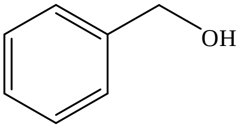
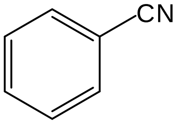
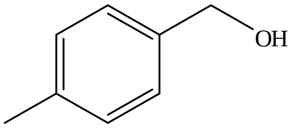
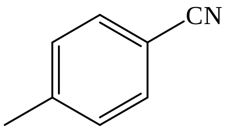
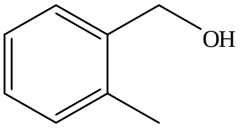
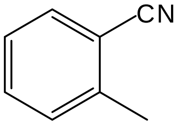
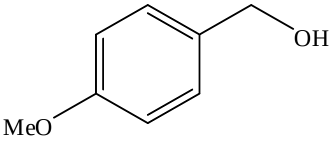
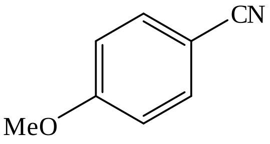
Using the optimized conditions, we next explored the scope and generality of the process (Table 3). It was found that benzylic alcohols carrying electron-donating and electron-withdrawing groups could be smoothly converted into the desired products with moderate to excellent yields. Primary benzylic alcohols with a variety of substituents at *ortho* position afford the corresponding nitriles in moderate yields. Electron-donating and electron-withdrawing groups, ranging from −OMe to $-CF_3$ and $-NO_2$ groups, were all well tolerated in the reactions. Polycyclic or heteroaromatic alcohols, such as naphthalen-1-ylmethanol (Table 3, entry 18) and furan-2-ylmethanol (entry 16), underwent effective conversion into the nitriles, and oxidation of 1,3-phenylenedimethanol (entry 20) afforded 1,3-dicyanobenzene in high yield. The allylic alcohol, cinnamyl alcohol (entry 19) afforded α,β-unsaturated nitriles in good yields. It has been observed in alcohol oxidation reactions, aliphatic substrate was less reactive and corresponding nitrile was obtained by increasing the PS-BHA-Cu catalyst loading.

Table 3: Polymer supported copper (II) catalyzed aerobic oxidative synthesis of aryl nitriles.

Entry	Substrate	Product	Yield (%)
1			94
2			96
3			90
4			98

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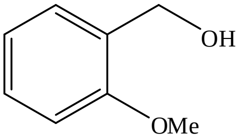
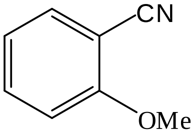
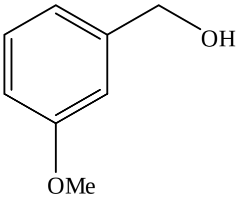
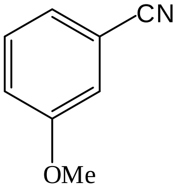
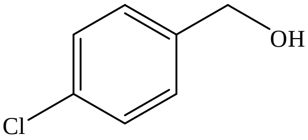
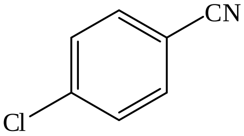
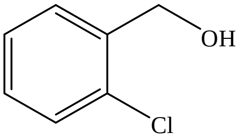
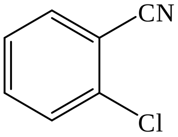
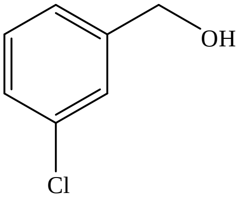
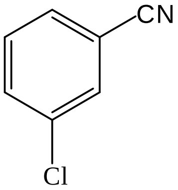
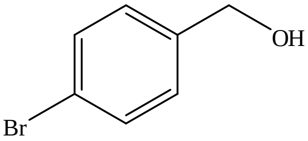
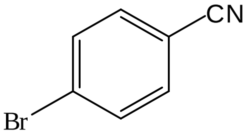
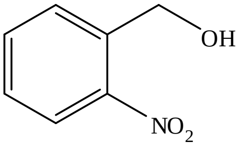
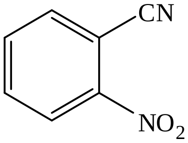
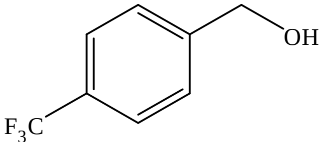
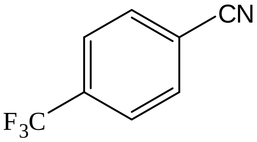
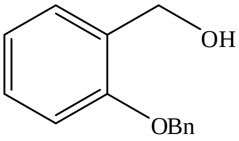
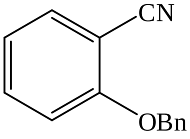
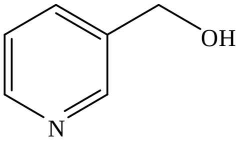
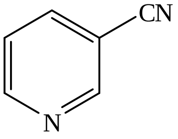
5			80
6			83
7			86
8			80
9			82
10			87
11			66
12			74
13			79
14			91

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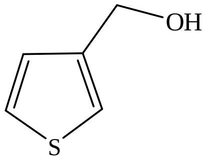
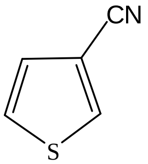
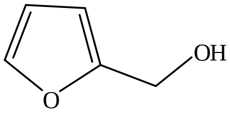
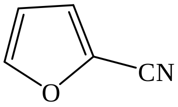
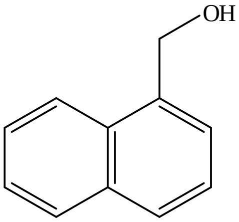
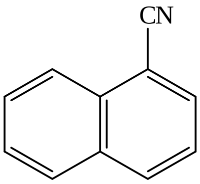
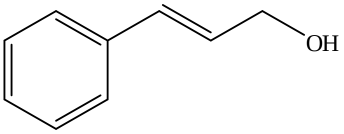
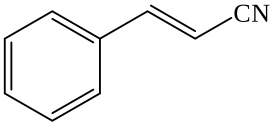
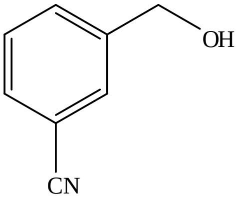
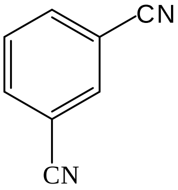
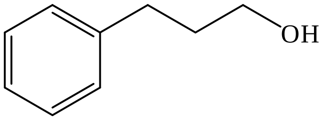
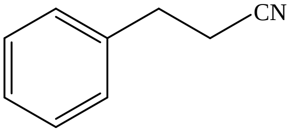
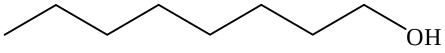
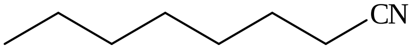
15			68
16			74
17			93
18			95
19			88
20			8
21			6

Reaction conditions: alcohol (0.5 mmol), PS-BHA-Cu (0.05 mmol), K_3PO_4 (0.05mmol), $HCOONH_4$ (2.0 mmol) ACN (3 mL), O_2 (1 atm.), Temperature (115 ^{0}C), 16 h.

Oxidative synthesis of primary amides from primary alcohols

In continuation of our interest in oxidative reactions, we were in search of a high-yielding, catalytic, cheap and environmentally benign system for oxidative synthesis of primary amides from primary alcohols. When TBHP and NH_3 (aq) was added to benzyl alcohol then the benzamide was the major product instead of benzonitrile under the reaction conditions.

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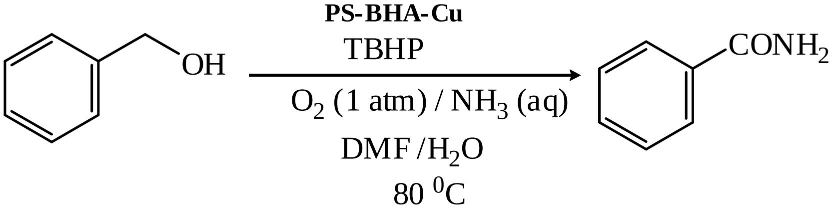

Scheme 4: Aerobic oxidative synthesis of bezamide from benzyl alcohol

We found that PS-BHA-Cu / TBHP system gave the amide as the major product (scheme 4). For example, when the amidation of benzyl alcohol was carried out using aqueous ammonia (25 wt%, 2.6 equiv. with respect to benzyl alcohol) and O_2 (1 atm) at 80 ^{0}C then benzamide was obtained in 94% yield along with benzonitrile 6%. N,N-dimethylformamide (DMF) was good solvent likely due to the high solubilities of benzyl alcohol, ammonia, and water (Table 4). Toluene and dichloromethane gave lower conversion of benzyl alcohol. Thus, we subsequently carried out the amidation in DMF medium. Next, the amidation of benzyl alcohol was carried out with various ammonia sources (Table 4). Besides aqueous ammonia, NH_4HCO_3 and $(NH_4)_2CO_3$ could act as effective nitrogen sources for the present amidation and gave benzamide in 81% and 73% yields, respectively.

This oxidative amidation was found to be sensitive to the reaction temperature. At lower temperatures (40-60 ^{0}C) only low to moderate yield was obtained. A reaction temperature of 80 ^{0}C was found to be optimal for the model reaction. The amount of pressure of molecular oxygen was varied from 1 atm to 2 atm, 1 atm oxygen pressure resulted in 99% conversion at 80 ^{0}C temperature. When oxygen pressure was raised to 2 atm the conversion and selectivity towards amide remained same. Therefore, 1 atm oxygen pressures were found to be optimum.

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Table 4: Effect of various nitrogen source and temperature

Entry	Nitrogen source	Temperature (^{0}C)	Yield (%)
1	NH_3 (aq)	80	94
2	NH_4HCO_3	80	81
3	$(NH_4)_2CO_3$	80	73
4	NH_3 (aq)	40	53
5	NH_3(aq)	50	61
6	NH_3 (aq)	60	74
7	NH_3 (aq)	70	85

Reaction conditions: alcohol (3 mmol), PS-BHA-Cu (0.05 mmol), TBHP (0.05mmol), 25% NH_3 (aq.) (9 mmol), DMF (3 mL), H_2O (1 mL), 5 h.

The scope of the present PS-BHA-Cu catalyzed amidation of primary alcohols was next examined. Herein, the scope is much extended to various kinds of structurally diverse primary alcohols. The amidation of benzylic alcohols, which contain electron-donating as well as electron-withdrawing substituents at different positions, efficiently proceeded to afford the corresponding substituted benzamide derivatives in excellent yields. The reaction rates for the amidation of *ortho*, *meta* and *para*-substituted benzyl alcohols were almost the same, and the corresponding substituted benzamides were obtained. 4-(Methylthio)benzamide was produced in 94% (Table 5, entry 18) yield from the corresponding 4-methylthiobenzyl alcohol without the oxidation of sulfur. The numbers of electron withdrawing groups at different positions were tested as well; the benzyl alcohols were converted into primary amides in good yields (Table 5, entries 7-14). Additionally, various heterocyclic amides were produced to prove the generality of this methodology (Table 5, entries 15-19). Not only pyridines and thiophene, but also furan can

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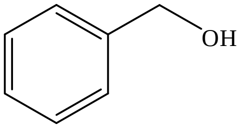
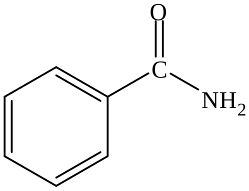
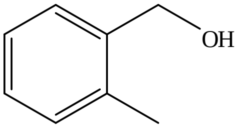
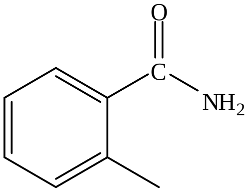
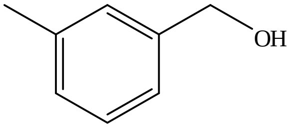
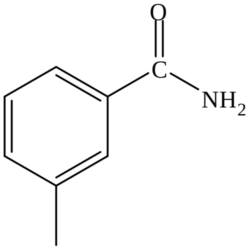
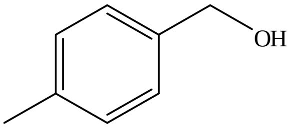
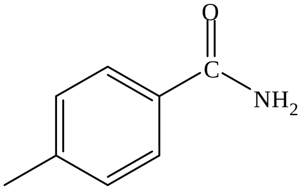
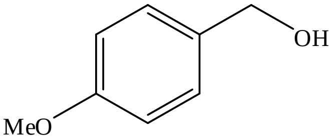
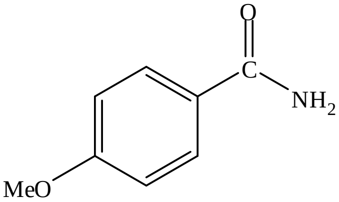
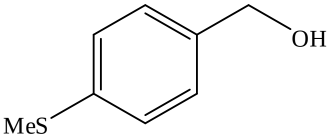
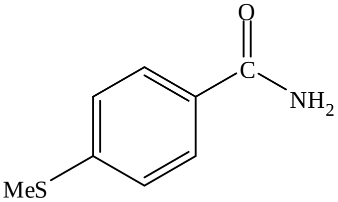
be tolerated. In the amidation of aromatic allylic alcohol such as cinnamyl alcohol derivative, the corresponding aromatic unsaturated amide could be obtained in excellent yields (90% yields).

Table 5: Polymer supported copper (II) catalyzed aerobic oxidative synthesis of aryl amides.

Entry	Substrate	Product	Yield (%)
1			94
2			89
3			96
4			94
5			98
6			95

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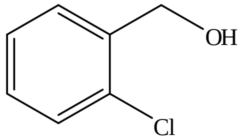
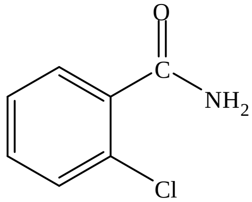
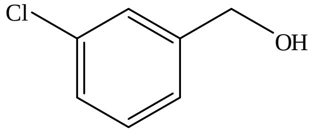
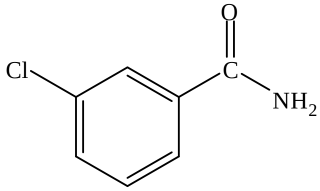
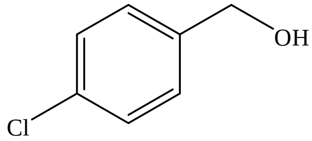
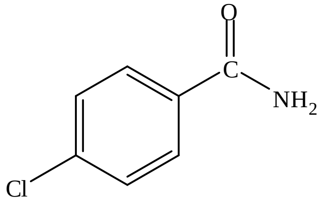
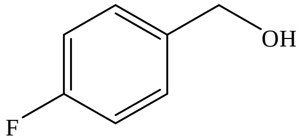
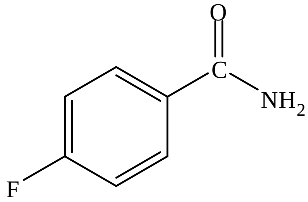
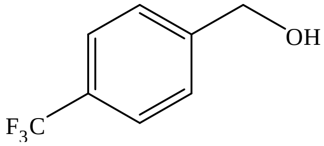
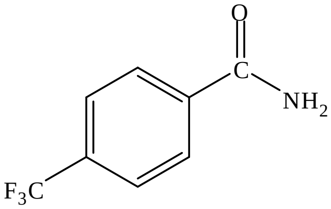
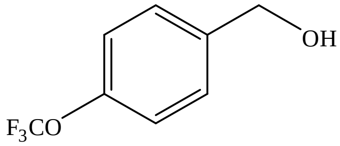
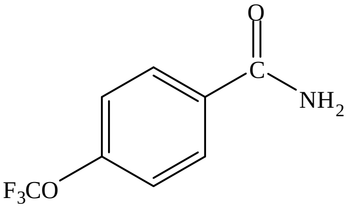
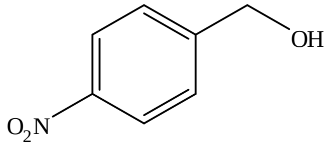
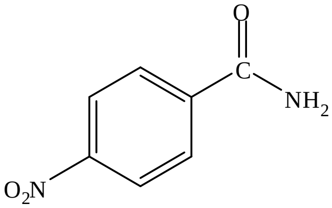
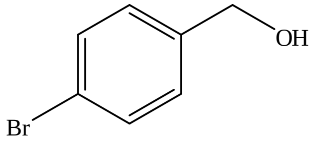
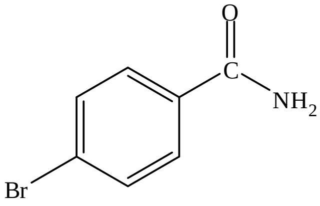
7			86
8			95
9			97
10			98
11			99
12			98
13			98
14			97

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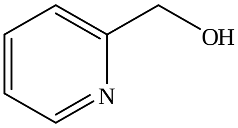
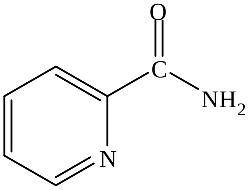
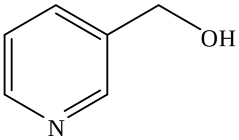
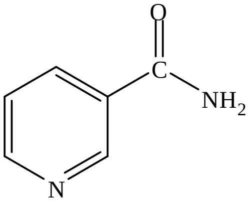
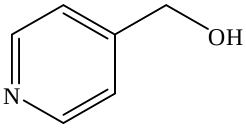
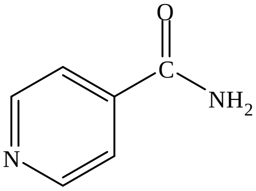
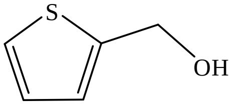
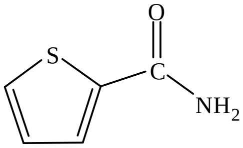
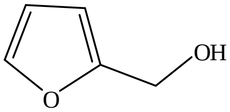
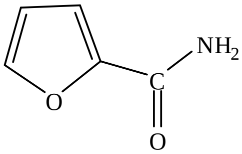
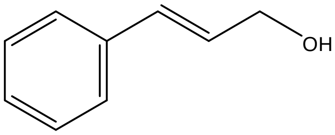
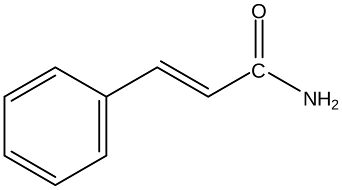
15			87
16			91
17			93
18			94
19			88
20			90

Reaction conditions: Reaction conditions: alcohol (3 mmol), PS-BHA-Cu (0.05 mmol), TBHP (0.05 mmol), 25% NH_3 (aq.) (9 mmol), DMF (3 mL), H_2O (1 mL), O_2 (2 atm.), 5 h.

Recycling of catalyst

The catalyst remains insoluble in the present reaction conditions and hence can be easily separated by simple filtration followed by washing. The catalyst was washed with methanol and dried at 100 ^{0}C. The oxidative synthesis of benzonitrile and benzamide from benzyl alcohol was carried out with the recycled catalyst under the optimized reaction conditions. The catalyst was recycled in order to test its activity as well as stability. The obtained results are presented in Fig.

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6. 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. Similarly, recycling of the catalyst was tested for the oxidative amidation of benzyl alcohol. No appreciable change in conversion as well as selectivity indicates that the catalyst can be reused.

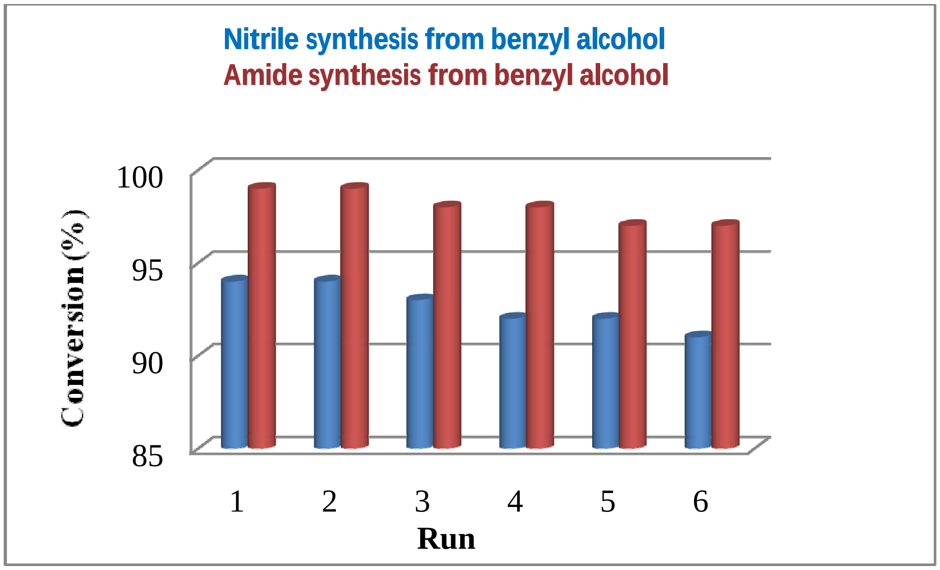

Fig.6. Recycling efficiency of PS-BHA-Cu for the benzonitrile and benzamide synthesis from benzyl alcohol

Conclusion

In the present work, we have developed and characterized an efficient polymer anchored copper Schiff base complex as the catalyst for the selective aerobic oxidative synthesis of aryl nitriles and primary aryl amides from benzylic alcohols and molecular oxygen as an oxidant. This catalyst also shows excellent catalytic activity in oxidative amidation reaction of benzylic alcohols. The present procedure is simple, efficient and environmentally benign allowing for a practical route to aryl nitriles and amides. The low cost of the catalytic copper system give this method potential to production on an industrial scale. Another important factor is the stability and recyclability of the catalyst under the reaction conditions used. This heterogeneous catalyst

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shows no significant loss of activity in the recycling experiments. The active sites do not leach out from the support and thus can be reused without appreciable loss of activity, indicating that the anchoring procedure was effective. The reusability of this catalyst is high and can be reused six times without significant decrease in its initial activity. We hope that the present catalytic system has a bright future in industrial application.

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