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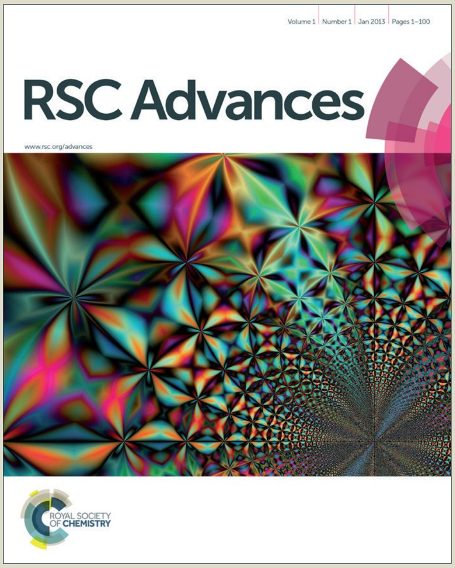

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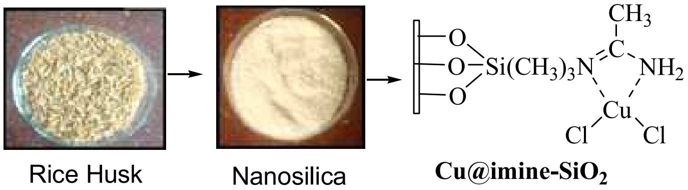

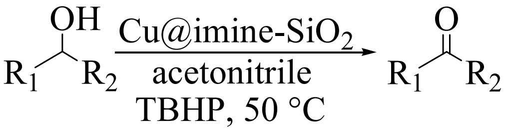

Rice Husk Derived Nanosilica Supported Cu (II) Complex: An Efficient Heterogeneous Catalyst For Oxidation Of Alcohols Using TBHP

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Abstract: We have developed a heterogenized catalyst of Cu(II) complex immobilized onto nanosilica obtained from rice husk (RH), through coordination of imine, generated via Schiff-base condensation between 3-aminopropyltriethoxysilane (APTES) functionalized nanosilica and acetamide. The synthesized catalysts were characterized by FT-IR, XRD, BET surface area measurements, ESR, SEM-EDX and ICP-AES. The synthesized catalyst showed excellent activity towards controlled oxidation of different primary and secondary alcohols in the presence of *tert*-butyl hydrogen peroxide (TBHP). Furthermore, the catalysts could be recovered by simple filtrations and can be reused upto many consecutive cycles without loss in activity.

Keywords: Nanosilica, Rice Husk, Alcohol Oxidation, TBHP, Cu@imine-nanoSiO_2

1. Introduction:

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most significant functional group transformations in organic synthesis that has got several industrial and academic applications. Traditionally, stoichiometric oxidants such as manganese and chromium oxides[1] are necessary to mediate this key conversion, sometimes producing almost the same amount of oxidant-derived waste. Moreover, various reports were available for the transition metal catalyzed oxidation reactions of alcohols such as Fe[2, 3, 4] Mo[5], Ru[6,7], Pt[8], Pd,[9,10,11] Vanadium[12,13], polyoxometalates[14], Mn[15], Os[16]etc., using molecular oxygen or H_2O_2 or TBHP as oxidizing agent. Nevertheless, a homogeneous catalytic system suffers from a number of drawbacks like separation of the catalyst from the product and rarely the catalyst is reused. Therefore, the development of catalytic system combining high catalytic effectiveness with easy recovery and reuse of the catalytic species is a topic of prime current interest. Solid supported transition metal catalysts have found immense interest in recent years for the development of new synthetic methodologies due to its high catalytic activity and reusability. Moreover, both copper(II) as well as copper(I) complexes[17,18] have been shown to be effective under homogeneous or heterogeneous condition for the oxidation of alcohols[19,20,21].Thus, efforts are being made to transform active homogeneous copper catalysts into effective heterogeneous catalysts by adopting various immobilization strategies utilizing solid supports like silica[22,23], clay[24], SBA-15/16[25,26] and zeolite[27] etc. Due to some specific characteristics of silica like low cost, wide accessibility, high thermal stability, and high surface reactivity, it is well known as one of the best supports for grafting of homogeneous metal compounds through coordinative linkage. Silica is one of the most valuable inorganic multipurpose compounds and naturally abundant oxides which are mainly made by synthetic means for its technological applications. In nature, silica is generally found in agro waste like rice husk (RH), which therefore can provide an alternating pathway to extract silica. It is well known that the silica content of the rice husk ash (RHA) can be as high as 90–97%[28].The surface of silica contains Silanol (Si-O-H) and Siloxane (Si-O-Si) groups which are the main keys of activity for any process taking place on the surface and which are considered to be non-reactive[29]. The silica obtained from rice husk ash (RHA) provides an abundant and cheap alternative source of silica which is useful for many applications particularly as a support for heterogeneous catalysis [30, 31].

In the present work, we have used rice husk (RH) derived nanosilica having high surface area and high reactivity prepared by reported method[32,33,34,35,36]. This nanosilica shows strong and a large number of acidic sites in comparison with commercial silica, making it a good support material to prepare copper immobilized catalyst to carry out oxidation of alcohols.

2. Experimental Section:

2.1 General Information:

All chemicals were obtained commercially and used as received without further drying or purification. The characterization of silica supported materials can be carried out only by some limited techniques such as FT-IR, ESR, XRD, SEM-EDX, ICP-AES, Brunner Emmet Teller (BET) surface area analysis only. This is because of the insolubility of the silica supported metal complexes in all common organic solvents.

X-ray diffraction pattern (XRD) of silica and nanosilica were recorded on a Bruker AXS D8 Advance Diffractometer with Cu-K (1.541A^0 radiation). FT-IR spectra were recorded in KBr pellets on a Shimadzu IR prestige-21 FT-IR spectrophotometer (200–4000 cm^{-1}). ESR spectra of the catalysts were recorded at liquid N_2 temperature at SAIF, IIT Bombay. The Cu loading in the catalyst were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on a Thermo Electron IRIS Intrepid II

XSP DUO. GC –MS was performed on an Agilent Technologies GC system 7820 coupled with a mass detector 5975 and SHRXI–5MS column (15 m length, 0.25 mm inner diameter and 0.25 micron film thickness).^{1}H spectra were recorded in $CDCl_3$ using TMS as an internal standard on a BruckerAvance 400MHz spectrometer. The specific surface areas were calculated following BET procedure. $CuCl_2.2H_2O$ is from Arora Matthy Ltd**.,** acetamide and *t*-butyl hydroperoxide (TBHP) from MERCK, hydrogen peroxide (H_2O_2), APTES (3-aminopropyltriethoxysilane) were purchased from Sigma Aldrich.

2.2 Methods

2.2.1 Synthesis of materials: To prepare the silica supported catalysts, first we have prepared the nanosilica from rice husk (RH) [32,33,34,35,36].The method of extraction of nanosilica from rice husk involves mainly four steps which are as described below:

(i) **Washing and drying**: Firstly, the RH is washed with water in order to remove impurities like dust, sand etc. associated with it. It is then dried in oven at 110ºC for 24 hours. The dried RH is refluxed with 1M HCl for about 90-100 minutes under stirring condition. This RH is then decanted and washed with warm distilled water to make it acid free followed by heating in oven at 110ºC for 20 hours.

(ii) **Heating**: A known quantity of RH which come across the above treatment is heated at 700ºC for 2.5 hours after which white coloured rice husk ash (RHA) is obtained.

(iii) **Extraction of silica**: For this purpose, 10 g RHA is stirred with 50 mL NaOH (2.5 M) solution in a beaker and heated at 70-80ºC for 3 hours followed by filtration. The residue so obtained is washed with 20 mL boiled water. After then, 10M H_2SO_4 added to make its pH equal to 2 followed by addition of NH_4OH to make its pH equal to 8. The precipitate is allowed to dry in oven after which white coloured silica is obtained.

(iv) **Extraction of nanosilica**: At last, the extracted silica is refluxed with 6 M HCl for 4 hours and washed to make it acid free. To this, 2.5 M NaOH is added and stirred for 1 hour. 10 M H_2SO_4 is added to this solution to make the pH of the solution equal to 8. The precipitate so obtained is washed with warm water and dried in oven for 2 days to get white coloured nanosilica.

Here we would like to highlight some images of rice husk materials involved in the preparation of nanosilica (fig 1.).

(a) (b) (c) (d) (e) (f)

Fig.1: (a) Rice Husk (RH), (b) Acid treated rice husk, (c) RH on burning in presence of air, (d) RH when burnt in a furnace at 700 ^{o}C, (e) Silica, (f) Nanosilica

2.2.2 Synthesis of Cu@imine-nanoSiO$_2$catalyst:

Step I: Synthesis of APTES functionalized silica gel: APTES@nanoSiO$_2$

3.8 g of nanosilica (dried at 120^{o}C for 2h) was added to 100 mL of dry toluene followed by addition of 2.0 mmol of APTES. The resultant mixture was refluxed under N$_2$ atmosphere for 6h and was allowed to cool. The solids were separated by filtration and washed repeatedly through Soxhlet extraction with toluene. The resulting material was then dried at 120^{o}C for 24 h to obtain APTES immobilized silica.

Step II: Synthesis of imine functionalized silica gel: imine@nanoSiO$_2$

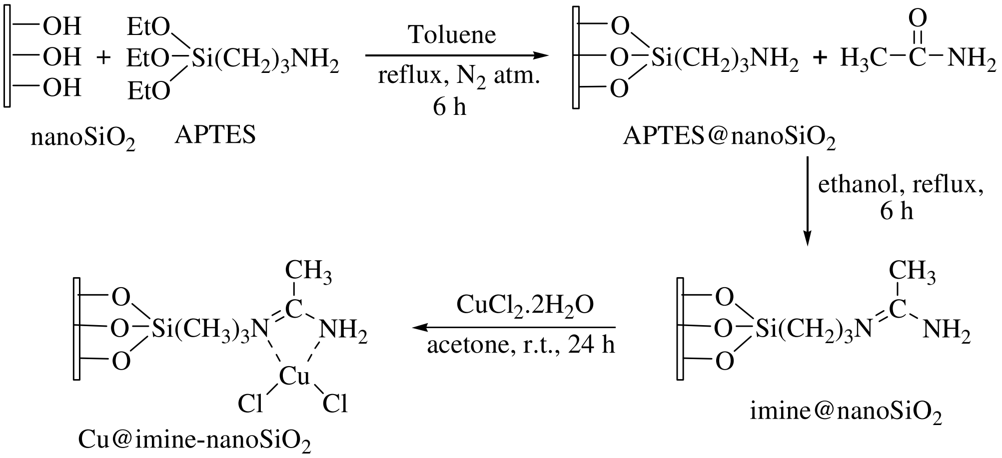
In a suspension of 2.3 g of APTES@nanoSiO$_2$ in 60 mL ethanol, 2.12 mmol of acetamide was added in small portions and the reaction mixture was refluxed for 6 h. The solids were separated from the solvent by filtration and washed repeatedly through Soxhlet extraction with ethanol and acetone. The resulting acetamide grafted silica was dried at 120 ^{o}C for 24 h and designated as imine@nanoSiO$_2$.

Step III: Immobilization of CuCl$_2$ .2H$_2$O on to imine@nanoSiO$_2$: Cu@imine-nanoSiO$_2$

2g of imine@nanoSiO$_2$ was added to a solution of 60 mg CuCl$_2$.2H$_2$O in 40 mL of acetone and the reaction mixture was stirred at room temperature for 24 h. The resulting solution was filtered off and the solids were washed several times through Soxhlet extraction with acetone. The material was designated as Cu@imine-nanoSiO$_2$ [37]. The reaction involved was given in the Scheme 1.

2.2.3 Typical procedure for oxidation of different primary and secondary alcohol using copper complex:

A 50 mL round-bottom flask was charged with a mixture of alcohol (1 mmol), catalyst (15 mg, Cu 0.26 mol %), oxidant and solvent (4 mL). The mixture was stirred at 50^{o}C temperature for the required time. After completion, the catalyst was subjected to centrifugation and the residual solid after filtration was washed with the same solvent (4 mL) for three times. The filtrate was diluted with water (10 mL) and extracted with ether (3×10 mL).



Scheme 1. Preparation of the supported Schiff base Cu(II) complex

The resultant organic phases was washed with brine (2×10 mL) and dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (ethyl acetate-hexane, 2:8) to obtain the desired products. For recycling experiments, residue catalyst after filtration was washed with excess water (3×5 mL) and diethyl ether (3×5 mL) in sequence. After drying the recovered catalyst at 100 °C overnight in an oven, the residual catalyst was subjected to subsequent run of the oxidation reaction by charging with the required amount of substrates (alcohol), oxidant and solvent, without further addition of catalyst. The isolated products were confirmed by comparing their FT-IR, ^{1}H NMR and mass spectral data with that of reported samples.

3. Results and discussion:

3.1 Characterization of the materials:

3.1.1 XRD of silica and nanosilica: Figure 2 shows XRD analysis of silica obtained from RH, in which sharp peaks appear indicating the crystalline nature of silica. Again, Figure 3 shows XRD pattern of nanosilica extracted from silica calcinated at 700 ^{o}C. The sample is amorphous as a broad diffraction peak around $2\theta \sim 21.8^o$ was obtained. These results agree with those obtained in the previously reported studies [32].Similarly, Figure 4 represents the XRD of Cu@imine-nanoSiO$_2$ which shows some sharp peaks similar to silica showing the crystallinity of the silica framework in presence of Cu(II)imine complex. Though there is similarity in the XRD profiles of SiO$_2$ and Cu@imine-nanoSiO$_2$, there intensity of the peaks differs as observed from Fig. 2 and Fig. 4, respectively. This change in the peak intensity of nanosilica after immobilization has altered the nano-SiO$_2$ surface resulting the modification of its crystallinity. However, it is observed that the peak at 21.8° has higher intensity in case of Cu@imine-nanoSiO_2 compared SiO_2.

3.1.2 FT-IR study:

From the FT-IR spectra of silica, nanosilica and silica based materials, it is observed that the FT-IR spectra of silica and nanosilica (Fig. 5, 6) are almost similar. A band at 1626 cm^{-1} which corresponds to the OH bending vibration of water molecule present in the silica. The large sharp peak at 1103.33 cm^{-1} is due to the structural siloxane framework which is the asymmetric stretching frequency of Si-O-Si and 797.60 cm^{-1} is also due to symmetric stretching of the same. The band at 467.76 cm^{-1} is due to the bending frequency of Si-O-Si. A large broad band at 3455.62 cm^{-1} is due to OH stretching frequency.

When nanosilica is functionalized by APTES, a new band appears at 1540 cm^{-1} due to NH_2 bending mode, indicating successful grafting of APTES on to nanosilica (Fig. 7b). Interestingly, a new band at 1631 cm^{-1} appears due to C=N stretching of imine generated through Schiff base condensation between amine group of APTES@nanoSiO_2 and C=O group of acetamide (Fig. 7c). In FT-IR spectra of Cu@imine-nanoSiO_2, a band at 451 cm^{-1} and 326 cm^{-1} due to νCu-N and νCu-Cl respectively (Fig. 8d), confirming that Cu is coordinated through nitrogen and chlorine.

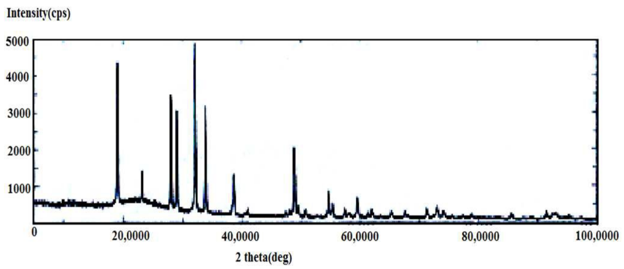


Fig.2: XRD of silica

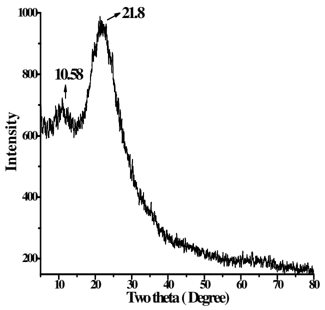


Fig. 3: XRD of nanosilica

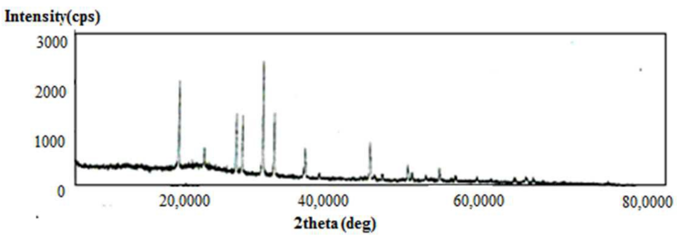


Fig 4 : XRD of Cu@imine-nanoSiO_2

3.1.3 BET analysis for surface area measurement:

The BET analysis for surface area measurements of the produced silica based materials are shown in Table 1. From our study, the surface area of nanosilica is found to be greater than that of silica and also the surface area of silica based materials decreased accordingly. The subsequent decrease is attributed to the successful immobilization of metal complex.

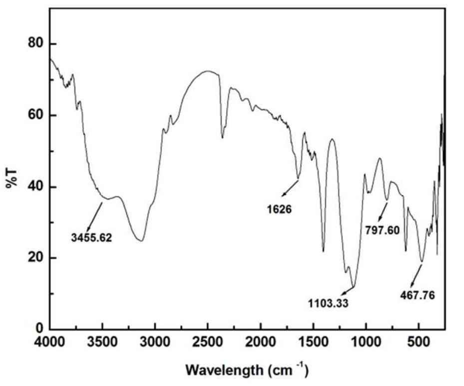


Fig.5: FT-IR spectra of silica

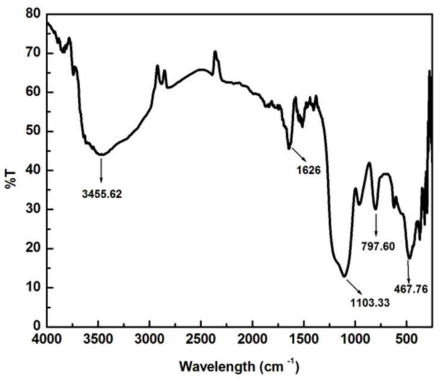


Fig. 6: FT-IR spectra of nanosilica.

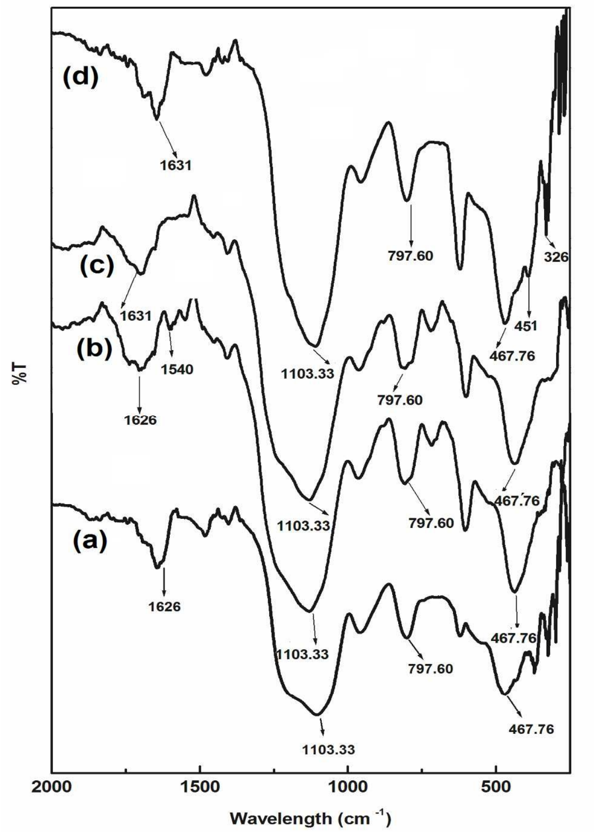


Fig.7: FT-IR spectra of (a) nanosilica (b) APTES@nanoSiO$_2$ (c) imine@nanoSiO$_2$ (d) Cu@imine-nanoSiO$_2$

Table 1:
BET measurement of silica and silica based materials

Entry	Materials	S_{BET} (m^2/g)
1	Silica	148.12
2	Nanosilica	189.97
3	APTES@nanoSiO$_2$	175.45

4	imine@nanoSiO_2	157.05
5	Cu@imine-nanoSiO_2	145.85

3.1.4 ESR, ICP-AES and SEM-EDX analysis:

The ESR spectra of the catalysts (Fig. 8) recorded at liquid nitrogen temperature in magnetically dilute form showed distinct signal for Cu(II) species showing four hyperfine lines with g-values of 2.19 ($g_{\|}$) and 2.04 ($g_{\perp}$) indicating tetragonal distortion as expected.

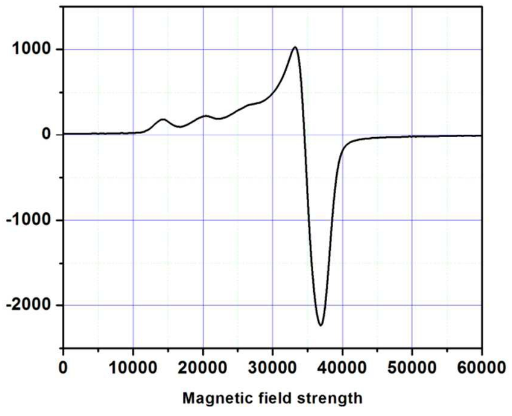


Fig. 8: ESR spectra of Cu@imine-nanoSiO_2

Considering the results of the ICP-AES and SEM-EDX observations, we are able to determine the metal attachment on the surface of solid supports. The amount of metal content in the Cu@imine-nanoSiO_2 catalyst is determined by ICP-AES analysis and is found to be 0.26 mol% per 15 mg of the catalyst. A comparison of EDX analysis (fig.9a, 9b) of nanosilica with Cu@imine-nanoSiO_2 confirms the presence of copper to the catalyst, which indicating the formation of metal complexes with the anchored ligand The SEM images (Fig. 10a, 10b) of nanosilica and the immobilized copper on nanosilica (Cu@imine-nanoSiO_2) clearly indicates the changes in the morphologies of the catalyst after introduction of metals were observed by SEM images.

4. Cu@imine-nanoSiO_2 catalyzed alcohol oxidations:

4.1Catalyst screening and solvent optimization

To investigate the effectiveness of the copper complex in oxidation reaction, 1-phenylethanol was chosen as a model substrate. Reactions were performed under different reaction conditions and results are summarized in Table 2. Initially, we carried out the oxidation reaction by treating 1-phenylethanol (1 mmol) with copper 0.26 mol% using H_2O_2 or TBHP as oxidant in various solvents at 50 °C. Generally, solvent plays a significant role in the conversion and product distribution of alcohol oxidation reaction. In order to investigate the effect of solvent for oxidation reaction, different solvents such as H_2O, MeOH, THF, CH_2Cl_2, toluene, acetonitrile and solvent-free condition were chosen for oxidation of 1-phenylethanol (Table 2, entries 1-10).

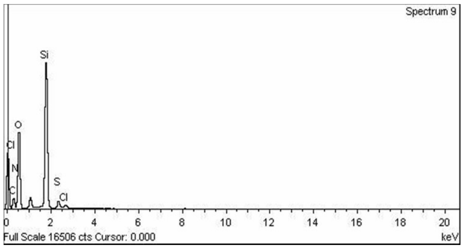
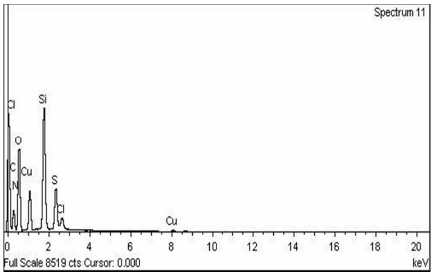
	

Fig. 9a: SEM-EDX of nanosilica	Fig. 9b : SEM-EDX of Cu@imine-nanoSiO_2

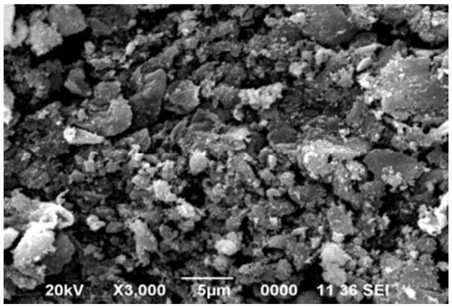
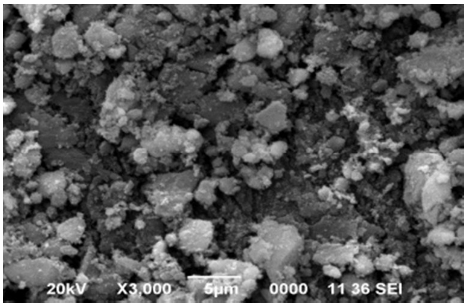

	

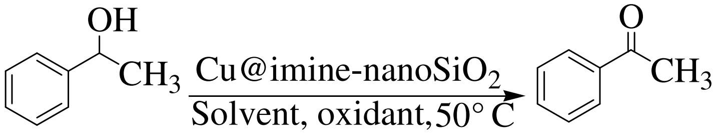
Fig.10a: SEM image of nanosilica	Fig.10b: SEM image of Cu@imine-nanoSiO_2

On study the effect of solvents, we have observed that, acetonitrile is the most suitable solvent for the reaction than the other solvents (Table 2, entry 9). Acetonitrile is polar and have a very high dielectric constant with a polarity index of 5.8. So, it may readily dissolve TBHP along with other organic substrates (reactants). This facilitates the adsorption of reactants on the active site of the catalyst and increases the effectiveness of the conversion and selectivity. Although, water has a high polarity index of 9.0, the conversion of 1-phenylethanol is lower than that of acetonitrile. It is due to its poor solubility in the reaction medium [38,39,40]. In solvent-free condition, the yield of product is trace amount (Table 2, entry 10).

The effect of catalyst amount on oxidation of 1-phenyl ethanol was also investigated. The results shows that with decreasing of the amount of catalyst to 10 mg (0.18 mol%) the yield of product decreased, while increasing amount of catalyst to 20 mg (0.35 mol%) did not show any considerable effect on the reactivity (Table 2, entries 11, 12). Again, it was seen that the reaction gives lower yield at room temperature (Table 2, entry15). During the course of our study, H_2O_2 is found to be less effective than TBHP for oxidation reaction (Table 2, entries 1-6). Again, we found that 0.3 mL of TBHP was sufficient for the effective conversion. However, the reaction did not proceed in the absence of TBHP (Table 2, entry 16).

After the investigation of the effects of different parameters for the oxidation of 1-phenylethanol, as a standard substrate, the best conditions were chosen and various alcohols were oxidized in the presence of a catalytic amount of Cu@imine-nanoSiO$_2$ and TBHP as an oxidant at 50 °C in acetonitrile. Further study was performed to enhance the scopes of oxidation reactions in different substituted primary and secondary alcohols.

Table 2:
Optimization of oxidation of 1-phenylethanol[a]



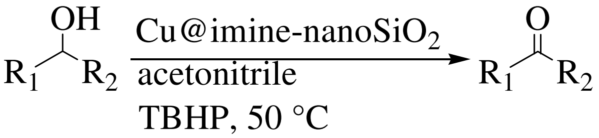
Entry	Solvent	Oxidant	Catalyst (mg)	Time (min)	Yield (%)[b]
1	H_2O	H_2O_2	15	180	33
2	MeOH	H_2O_2	15	180	41
3	CH_2Cl_2	H_2O_2	15	180	53
4	THF	H_2O_2	15	180	55
5	Toluene	H_2O_2	15	180	60
6	CH_3CN	H_2O_2	15	180	80
7	H_2O	TBHP	15	90	65
8	MeOH	TBHP	15	60	76
9	CH_3CN	TBHP	15	35	96
10	-	H_2O_2	15	180	trace
11	CH_3CN	TBHP	10	45	90
12	CH_3CN	TBHP	20	40	96
13	CH_3CN	TBHP	15	50	80[c]
14	CH_3CN	TBHP	15	40	97[d]
15	CH_3CN	TBHP	15	150	60[e]
16	CH_3CN	-	15	180	-

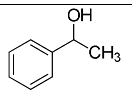
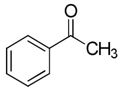
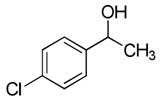
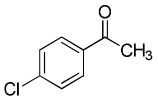
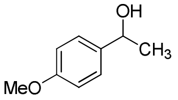
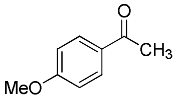
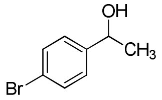
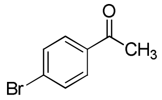
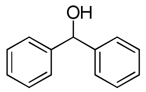
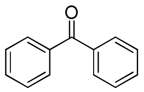
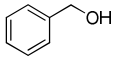
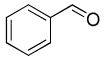
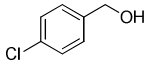
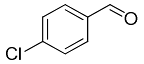
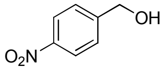
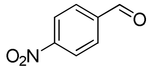
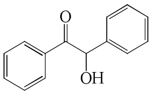
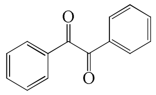
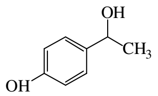
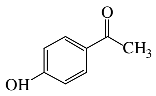
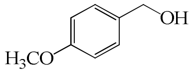
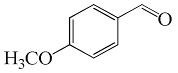
[a] Reaction conditions: 1-phenyl ethanol (1 mmol), oxidant (0.3 mL), solvent (4 mL), Cu@imine-nanoSiO$_2$ (15 mg, 0.26 mol% Cu) ca. 50 ºC in air unless otherwise noted. [b] Isolated yield. [c] TBHP (0.1 mL) [d] TBHP (0.5 mL). [e] r.t (5h).

Both the primary and secondary alcohols on oxidation gave satisfactory to good yields of the corresponding aldehydes and ketones, although a significant variation in yields was noticed. The results are summarized in Table 3. It has been seen from Table 3 that, in general secondary alcohol was also found to be more reactive toward oxidation under the same reaction condition.

Table 3

Oxidation reactions of various alcohols using TBHP and Cu@imine-nanoSiO$_2$catalyst[a]



Entry	Alcohol	Product	Time (min)	Yield(%)[b]
1			35	96
2			35	98
3			30	97
4			30	97
5			30	95
6			5	67
7			5	69
8			10	69
9			30	80
10			20	75
11			25	78
12	$CH_3-(CH_2)_6-CH_2OH$	$CH_3-(CH_2)_6-CHO$	15	90

[a] Reaction conditions: alcohol (1 mmol), oxidant (0.3 mL), solvent (4 mL), Cu@imine-nanoSiO$_2$ (15 mg, 0.26 mol% Cu) ca. 50 ºC in air unless otherwise noted. [b] Isolated yield. Formation of product was confirmed by comparing FT-IR; 1H & 13C NMR spectra, GC-MS and melting point measurement.

Both electron withdrawing and electron donating substituents, such as p-Cl, p-NO_2, p-Br, p-MeO, p-Me in the benzene ring gave the desired products in 69–98% yield (Table 3, entries 1–8). Primary benzyl alcohols with electron donating and withdrawing groups gave products in good yields (Table 3, entries 6-8). Primary benzyl alcohols bearing halogen group was also successfully oxidized to benzaldehyde with satisfactory yields (Table 3, entry 7).

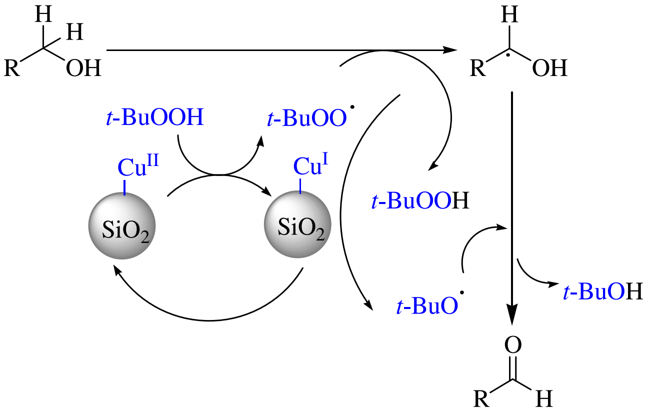
4.2 Reuse of the catalysts:

Reusability of a catalyst is an important and attractive criterion for eco-friendliness, efficiency and industrial relevance. Therefore, we studied the reusability of the catalyst up to 5th cycle using 1-phenylethanol as model substrate (Table 4). The reusability tests were done by simple filtration of the reaction mixture. For this purpose, after completion of the reaction, the catalysts were separated from the reaction mixture by centrifuging and then the catalysts were dried in an oven. After drying, it was again used for alcohol oxidation following the same procedure as mentioned above. It was found that the yield of the product goes on decreasing as the number of cycle increases. The slight decreasing trend of the product formation was due to physical loss of the nanosilica supported Cu@imine-nanoSiO_2 complex during separation and purification. Again, it was observed that, the reaction time goes on increasing with increase of number of cycle as shown in the table 4.

Table 4:
Recycling of the catalyst for the oxidation reaction

No. of cycle	Time (min)	% yield
1	35	96
2	45	94
3	50	90
4	65	88
5	65	85

Finally, a probable mechanism of the alcohol oxidation reaction has been proposed which is as given below in the scheme 2



$$\mathrm{Cu^{II}} + t\text{-BuOOH} \longrightarrow \mathrm{Cu^{I}} + t\text{-BuOO}^{\bullet} + \mathrm{H^{+}}$$

$$\mathrm{Cu^{I}} + t\text{-BuOOH} + \mathrm{H^{+}} \longrightarrow \mathrm{Cu^{II}} + t\text{-BuO}^{\bullet} + \mathrm{H_2O}$$

Scheme 2: Plausible mechanism of the alcohol oxidation

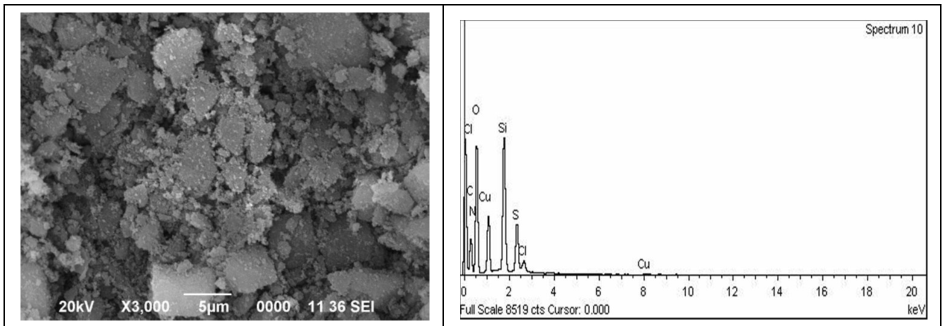


Fig. 11: SEM-EDX spectra Cu@imine-nanoSiO_2 after 5th use

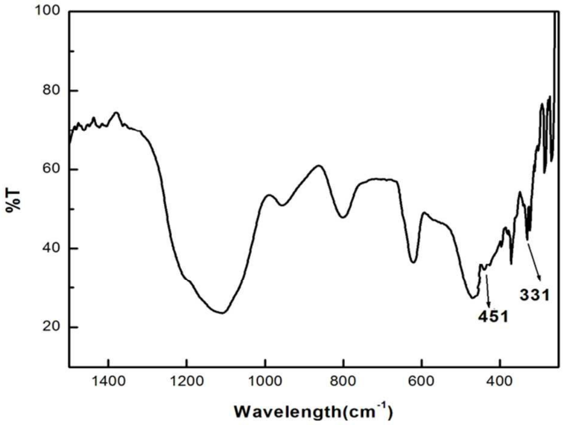


Fig.12: FT-IR spectra of Cu@imine-nanoSiO_2 after 5th cycle

To gain better insight into how our catalytic system changes during the reaction, we have also studied the catalytic evolution by means of SEM and energy dispersive X-ray analysis (EDX). Interestingly, inspection of the SEM image of a sample of catalyst after 5th cycle from the alcohol oxidation reaction indicates the immobilization of copper metal onto nanosilica based materials *i.e.* the recovered catalyst showed almost the similar SEM image like the fresh catalyst. Furthermore, on the basis of the results of the EDX spectra, Cu seems to be present on the surface of solid support. Moreover, the IR spectra of the used catalyst also indicates no shift in any major peak, regarding to Cu-N and Cu-Cl bands.

Table:5 Comparative results for the oxidation of alcohols using reported conditions with the present method

Entry	Metal Catalyst	Condition	Yield/ conversion	reference
1	$CuAl_2O_4$-CCM and $CuAl_2O_4$-MCM.	Acetonitrile, oxidants, time: 8 h, temp 80 °C.	65-99 % yield	[38]
2	Cu/HT (7.3 mol%), .	p-xylene, Ar, time: 4-24 h, temp 130-150 °C,	72-99% conversion	[41]
3	silica-supported palladium catalysts bearing N–N, N–S and N–O chelating ligands	Molecular O_2, K_2CO_3, time: 2.5- 15 h, 90 °C**.**	40-96% yield	[42]
4	$Cu_3(BTC)_2$	TEMPO, Na_2CO_3 , acetonitrile, 22 h, 75 °C, oxygen atmosphere	2-89 % yield	[43]
5	Cu@imine-nanoSiO_2	TBHP, Acetonitrile, time: 5-35 min, 50 °C	67-98 % yield	Present work

4.3 Metal leaching test

To verify the leaching of metal during the cycles, a metal leaching test was performed. The alcohol oxidation of 1-phenylethanol was started in the usual way. After completion of the reaction, the reaction mixture was subjected to centrifugation. The leach metal in the filtrate was determined by ICP- AES analysis and found to be 0.25 ppm Cu. These results suggest the strong coordination and stability of the metal framework which precludes the metal leaching during the reaction

In addition, the catalytic performance of Cu@imine-nanoSiO_2 was compared with some other reported ligand and metal systems (Table 5). The present procedure is effective for the oxidation of alcohols in a short reaction time and at low temperature so is applicable to a wide variety of functional groups

Conclusion:

In conclusion, we have developed a novel copper-based heterogeneous catalyst by immobilizing $CuCl_2.2H_2O$ onto imine-functionalized nanosilica coordination. From the environmental point of view, the extraction of silica from RH is safe, cost effective and environment friendly. Considering easy availability of RH worldwide, the production of nanosilica from RH can be utilized as low cost technology in fine chemical synthesis. The synthesized catalyst exhibited excellent activity for the selective and rapid oxidation of benzylic alcohols to the corresponding aldehydes and ketones. The reaction time is very fast and no over-oxidized product was observed. The catalytic system could be reused successfully upto fifth cycle without significant loss of activity or yield or extension of the reaction time. This methodology will find interest in both academic as well as industry due to its cost-effective process involving heterogeneous nanosilica.

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