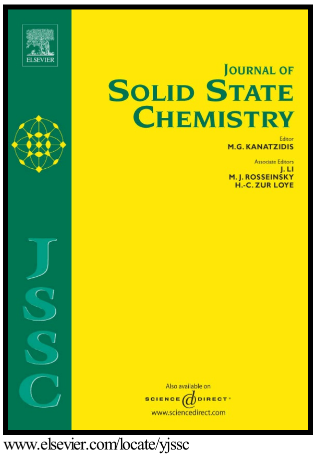

Silica functionalized Cu(II) acetylacetonate Schiff base complex: An efficient catalyst for the oxidative condensation reaction of benzyl alcohol with amines

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Silica functionalized Cu(II) acetylacetonate Schiff base complex: An efficient catalyst for the oxidative condensation reaction of benzyl alcohol with amines

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Abstract:

Silica functionalized Cu(II) acetylacetonate Schiff base complex *via* the one pot reaction of silica functionalized 3-aminopropyltriethoxysilane with acetyl acetone and copper acetate has been reported. The synthesized material was well characterized by analytical techniques such as FT-IR, UV-DRS, XRD, SEM-EDX, HR-TEM, EPR, ICP-AES and BET analysis. The characterization results confirmed the grafting of Cu(II) Schiff base complex on the silica surface. The catalytic activity of synthesized silica functionalized Cu(II) acetylacetonate Schiff base complex was evaluated through the oxidative condensation reaction of benzyl alcohol to imine.

Keywords:

Silica; Cu(II) acetylacetonate Schiff base complex; 3-Aminopropyltriethoxysilane; Oxidative condensation.

1. Introduction

In recent years, functionalization of silica material with metal complexes are very active area of research in the fields of organic synthesis, catalysis, adsorption, separation and sensing [1-5]. Because, these heterogenized metal complexes of their easy separation from the reaction mixture and minimal product contamination caused by metal leaching [6-9], as well as the recyclability of catalyst [10], it is well known that Schiff base metal complexes have been widely employed as an efficient catalyst in a variety of oxidation reactions [11-14]. Due to their environmental issue arises from homogeneous catalyst and newer development in chemistry, which cannot be well suitable for large scale process, recent researchers are very much interested in the transformation of homogeneous catalytic reaction into heterogeneous process. Generally, heterogeneous catalyst has been prepared by anchoring homogeneous catalysts onto insoluble supports like, metal oxides [15], aluminophosphates [16], MCM-41 [17], silica [18], SBA-16 [19], SBA-15 [20], montmorillonite [21], Zeolite-X [22], and zeolite-Y [23].

Oxidation of alcohols to the corresponding carbonyl compounds is one of the most important transformations in organic synthesis [24-26]. In particular, the oxidation of benzyl alcohol to benzaldehyde is an important organic reaction due to the widespread applications of benzaldehyde in perfumery, dyestuff and agro-chemical industries [27-29]. There are numerous methods available in the literature for the oxidation of benzyl alcohols to their corresponding benzaldehydes. Gao et al [30]. reported that functionalized dioxomolybdenum(VI) complex with bidendate Schiff base type CPS-[MoO_2(ALGl)$_2$] microsphere is efficient catalyst for the oxidation of benzyl alcohol to benzaldehyde From the background of this, herein we have reported the design and characterization of silica functionalised Cu(II) Schiff base metal complexes bearing acetyl acetone group. In addition, we have also studied the catalytic properties of these complexes in the oxidative condensation reaction of benzyl alcohol with variety of amines to corresponding Schiff bases.

2. Experimental

2.1. Materials and instruments

3-aminopropyltriethoxysilane (3-APTES) was procured from Sigma Aldrich and all the other reagents and solvents were purchased from Loba Chemie. FT-IR spectra of the samples were recorded in the region of 4000-400 cm^{-1} on Shimadzu spectrophotometer using KBr pellet technique. Diffuse reflectance spectra were obtained on an UV-DRS Ocean Optics px-2 spectrometer with pulsed xenon light source. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Mini Flex II diffractometer. The surface morphology of the synthesized material was analyzed by using High Resolution Transmission Electron Microscope (HRTEM, JEOL JEM 2100) scanning electron microscope (HRSEM, JSM 840A, JEOL.) equipped with EDX. ^1H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were taken in DMSO-d_6 or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane (^1H, ^{13}C). EPR spectrum was recorded on a JEOL model JES FA200 EPR spectrometer at liquid nitrogen temperature operating at X-band frequency (9.45 GHz). 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. BET Surface area was calculated by Brunauer Emmett and Teller Equation using multipoint adsorption in the P/Po range 0.05-0.33. Micro pore size distribution was calculated using Horvath-Kawazoe and BJH method. The Surface area has been measured by using Micromeritics ASAP 2020 surface area analyzer. The surface area analysis condition such as sample mass: 0.2478 g, analysis bath temp: -195 °C, degassing temperature and duration 150 °C & 12 h respectively.

2.2. Functionalization of silica gel with 3-aminopropyltriethoxysilane

Initially, the silica gel was activated by refluxing silica gel (3.0 g) with 6 mol L^{-1} HCl for 8 h. After cooling, solid was filtered off and washed with doubly distilled water until free of acid. After complete removal of acid, the crude solid was dried for 12 h in a furnace at 120 °C and finally the unwanted gases were removed by vacuum at 100 °C for 8 h. Then the amino functionalized silica gel (SiO_2-NH_2) was prepared by refluxing silica gel (3.0 g) with 3-aminopropyltriethoxysilane (10 mmol) in dry dichloromethane for 24 h. The resultant solid was filtered and washed three time with dichloromethane and dried under vacuum at 50 °C.

2.3. Preparation of silica supported Cu(II) Schiff base complex [SiO_2-NH_2-Cu(II)]

A mixture of acetyl acetone (10 mmol) and copper acetate (5 mmol) in ethanol (30 ml) was added to the suspended solution of amino functionalized silica gel (SiO_2-NH_2) (3.0 g) and the mixture was refluxed for 5 h. After cooling, the solid was filtered and washed with hot ethanol to remove the unreacted copper acetate. Finally, the resultant solid was dried under vacuum at 60 °C and labelled as SiO_2-NH_2-Cu(II) (Scheme 1).

2.4. General experimental procedure for the oxidative condensation reaction

A mixture of benzyl alcohol (1.5 equiv) and aromatic amine (1 equiv) in the presence of SiO_2-NH_2-Cu(II) complex (50 mg) as a catalyst in toluene (10 ml) was refluxed until the completion of the reaction as evidenced by TLC. After completion, the reaction mixture was cooled to room temperature and the catalyst was removed by simple filtration. Then the filtrate was evaporated under reduced pressure. The pure products were obtained by recrystallization of crude product with ethanol. The Product was confirmed by ^{1}H NMR Spectroscopy.

3. Results and discussion

3.1. Characterization of synthesized silica functionalised Cu(II) Schiff base complex

The synthesized silica functionalised Cu(II) Schiff base complex was completely characterized by FT-IR, UV-DRS, XRD, SEM-EDX, HRTEM and EPR, BET analysis.

3.1.1. FT-IR study

Fig. 1 Shows the FT-IR spectra of the activated silica (1a), amino functionalised silica (1b) and silica functionalised Cu(II) Schiff base complex (1c). In FT-IR spectra of activated silica, a broad band appeared at 3442 cm^{-1} was due to the symmetric stretching vibration of water molecule and the band appeared at 1651 cm^{-1} correspond to –OH bending vibration. The bands observed nearly in the region of 1085 and 804 correspond to the asymmetric and symmetric stretching vibrations of Si-O-Si, respectively. The band at 462 cm^{-1} correspond to the bending vibrations of O-Si-O groups present in the silica framework. Upon functionalization with 3-APTES, the intensity of the -OH band was decreased and a new band appeared at 1512 cm^{-1} corresponds to the bending vibration of NH_2 group which confirms the successful functionalization of 3-APTES on silica surface [31]. But, the FT-IR spectrum of SiO_2-NH_2-Cu(II) complex was something different than that of parent materials and showed two new bands at 1604 and 1512 cm^{-1} which may be attributed to the C=N stretching vibration and the band at 1739 cm^{-1} corresponds to the C=O present in the acetylacetonate ring of metal complex [32]. This indicates that the amino group present in functionalised silica was almost reacted with acetyl acetone to form a Schiff base. Moreover, some other peaks observed in the range of 1600-1340 cm^{-1} due to the C-O and C-N vibrations, indicates the formation of silica functionalized Cu(II) Schiff base complex.

3.1.2. UV-vis DRS

The electronic spectrum of pure SiO_2 showed three peaks at λ_{max} = 220, 260 and 334 nm (Fig. 2a). When the SiO_2 was functionalized with 3-APTES, we observed that the peak obtained for pure silica was shifted to the higher wavelength (238, 326 and 402 nm) with band broadening (Fig. 2b). But, in the case of silica functionalized Cu(II) Schiff base complex some additional peaks appeared at 442, 498 and 541 nm. This may lead to the charge transfer between the ligand and the metallic ion [33].

3.1.3. XRD Characterization

The XRD patterns of activated silica and silica functionalized Cu(II) Schiff base complex are shown in Fig. 3. The XRD pattern of pure SiO_2 exhibited a broad peak centred at $2\theta = 22.37°$ indicating the amorphous nature of the silica [34]. Whereas, silica functionalized copper(II) Schiff base complex showed a peak at $2\theta = 21.71°$ which suggests that there is only a small change in the centre of peak position but the intensity of the peak reduced slightly. It is clear from the XRD patterns, that there was essentially no major changes occurred during the functionalization of silica with Cu(II) Schiff base complex.

3.1.4. SEM –EDX and High resolution TEM analysis

The SEM images (Fig. 4a, 4b) of activated pure silica and the functionalized Cu(II) Schiff base complex clearly indicates the changes in the surface morphology of the catalyst before and after introduction of metal complex on silica surface. It was seen from the Fig. 4 that the morphology of the both samples are quite similar in appearance with well dispersed stone like structure. Fig. 4c & 4d shows different morphology compare to pure activated silica surface, its indicates that the Cu(II) complex bind with silica surface. This type of morphology to possess good catalytic behavior [35]. Furthermore, EDX spectrum of silica functionalized Cu(II) Schiff base complex (Fig. 4c,4d) confirms the presence of copper (Fig. 4e), which is in good agreement with the value determined by ICP-AES technique. The Cu(II) amount of the immobilized catalyst on SiO_2 was found to be 0.373 mmol g^{-1} or 50 mg.

The high resolution transition electron microscopy images of SiO_2 revealed that all the particles have stone like structure with well definite pore structure. (Fig. 5a, 5b) The TEM image of SiO_2-NH_2-Cu(II) complex shows a thick grey colour core and the surface region indicates the presence of inorganic Cu (II) moieties that completely cover the SiO_2 resulting the formation of SiO_2-NH_2-Cu (II) complex.

3.1.5. EPR spectroscopy.

EPR spectra also proved the presence of Cu(II) ion in the silica functionalized Cu(II) Schiff base complex. The EPR spectra of the powdered silica functionalized Cu(II) Schiff base complex was recorded on X-band at frequency 9.45 GHz and the $g_{||}$ & $g_{\perp}$ values were intended from the obtained spectrum. The calculated $g_{||}$ & $g_{\perp}$ values for the complex were found to be 2.27 and 2.05 indicating the formation of Cu(II) complex (Fig. 6) [32].

3.1.6. N_2 adsorption-desorption isotherm

The N_2 adsorption and desorption isotherms of SiO_2 and SiO_2-NH_2-Cu(II) complex are shown in Fig. 7. This study provided the information about the specific surface area and porosity of the prepared samples. The isotherms of both the samples followed typical type IV patterns according to IUPAC classification with a typical hysteresis loop, featuring mesoporous material with highly uniform pore size distribution [36] Cu(II) complex on porous supports shows decrease in its specific surface area and pore volume. The support SiO_2 shows a high surface area of $387 m^2 g^{-1}$; and pore volume of 0.4215 cm^3/g; after Cu(II) complex immobilization, the surface area and pore volume gets reduced to $151 m^2 g^{-1}$, respectively, with pore radius of 28Å and 18Å, respectively. A considerable decrease in the BET surface area, pore volume and pore radius suggested that Cu(II) complex have been anchored on the inner surface of the pores.

3.2. Catalytic properties

The catalytic activity of the silica functionalized Cu(II) Schiff base complex was evaluated for the oxidative condensation reaction of benzyl alcohol with different aromatic/aliphatic amines affording the corresponding imines in good yields (Scheme 2).

In order to optimize the suitable reaction conditions for this oxidative condensation reaction, we have chosen benzyl alcohol and aniline as model reactants. Initially, we have started our investigation under neat condition under refluxing toluene, where no reaction was observed to produce the corresponding product (Table 1, entry 1) even after prolonged time

(24 h). So we have added SiO_2-NH_2-Cu(II) complex (50 mg) as a catalyst, interestingly the reaction was going well and produce the corresponding product in excellent yields (94%) (Table 1, entry 5) in shorter time (10 h). Next, we have find out the suitable solvents for this reaction, same reaction was performed with different solvents (10 ml) like ethanol, methanol, dichloromethane, toluene, chlorobenzene, nitrobenzene and acetonitrile under refluxing conditions and found that toluene was most efficacious one in the terms of yield and time.

After that, we have to fix the amount of catalyst required for this reaction, we have carried out the reaction with different quantity of catalyst like 10 mg, 20 mg, 30 mg, 40 mg, 50 mg and 100mg. The reaction rate as well as product yield was increased with increasing the catalyst amount from 10 mg to 50 mg and decreases the reaction time. By increasing the catalyst above 50 mg, there is no change in reaction rate and yield. This optimization results suggested the 50 mg of catalyst and toluene were found to be most suitable for this reaction (Table 2).

Under this optimized conditions, differently substituted amines were made to react with benzyl alcohol and the results are summarized in Table 3.

From the table we noted that the aromatic amines having electron donating group required shorter reaction time to produce the corresponding product in better yield than that of electron withdrawing counter parts (Table 3, entries 3,4 and 9). Aliphatic amines also reacted well and provided the good yields (Table 3, entries 10 and 11).

Next, the reusability of the new SiO_2-NH_2-Cu(II) catalyst has been checked using the reaction of benzyl alcohol with aniline under optimized reaction conditions. After extracting the reaction mixture, the catalyst was recovered by simple filtration, washed twise with hot ethanol and dried. Then the recovered catalyst can be effectively reused for five consecutive runs with slight decrease in activity (Table 4).

The catalytic efficiency of the synthesized silica functionalized Cu(II) Schiff base complex was compared with the other earlier reported catalysts and the results are presented in the Table 5. From this comparison Table 3, we suggested that the efficiency of the SiO_2-NH_2-Cu(II) catalyst is comparable or better than the reported catalysts.

3.2.1. Plausible mechanism for the oxidative condensation reaction

A proposed mechanism for this reaction has given in (Scheme 3), in which the catalysts accept hydrogen from alcohols and oxidize them to aldehydes in the first step. In the second step, the carbonyl moiety undergoes condensation with arylamine and form azomethine functionality, ie. Imine compounds.

4. Conclusion

We have successfully synthesized the silica functionalized Cu(II) Schiff base complex bearing acetylacetone group in a stepwise manner. SiO_2-NH_2-Cu(II) complex was confirmed by FT-IR, UV-DRS, XRD, SEM-EDX, HR-TEM, EPR, ICP-AES and BET analysis. In addition, to this the material has been employed as an efficient heterogeneous catalyst for the oxidative condensation reaction of benzyl alcohol with aniline, resulting to high yield of imines compounds. Moreover the obtained catalyst could be recovered and reused for five times with slight decrease in activity.

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Scheme captions

Scheme 1: Synthesis of silica supported Cu(II) Schiff base complex [SiO_2-NH_2-Cu(II)].

Scheme 2: Oxidative condensation reaction of benzyl alcohol with amines.

Scheme 3: Plausible mechanism for the oxidative condensation reaction.

Figure captions

Figure 1: FTIR-Spectra of (a) SiO_2, (b) SiO_2-NH_2, (c) SiO_2-NH_2-Cu(II) complex.

Figure 2: UV-vis adsorption spectra of (a) SiO_2, (b) SiO_2-NH_2 and (c) SiO_2-NH_2-Cu(II)

Figure 3: X-ray diffraction patterns of patterns of SiO_2 and SiO_2-NH_2-Cu(II) complex

Figure 4: SEM images (a & b) SiO_2, (c & d) SiO_2-NH_2-Cu(II) complex, (e) EDX spectrum of SiO_2-NH_2-Cu(II) Schiff base complex.

Figure 5: HRTEM images (a) SiO_2, (b) SiO_2-NH_2-Cu(II) complex.

Figure 6: EPR spectrum of silica functionalized Cu(II) Schiff base complex.

Figure 7: N_2 Adsorption-Desorption isotherms and pore size distributions inset. Of: (a) activated SiO_2 and (b) SiO_2-NH_2-Cu(II) complex.

Table Captions

Table 1: Effect of solvents on oxidative condensation reaction[a].

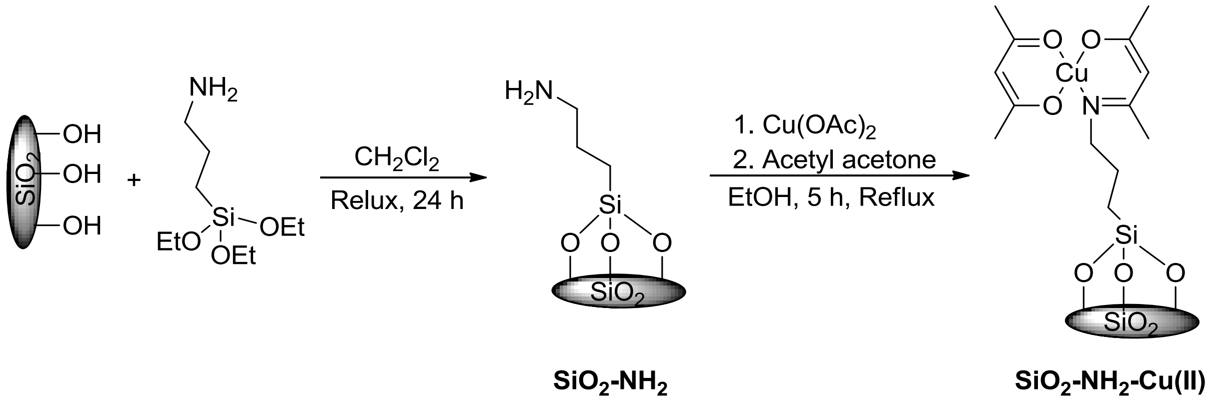
Table 2: Effect of catalyst amount and temperature.

Table 3: Substrate scope of oxidative condensation reaction[a]

Table 4: Reusability of the catalyst[a]

Table 5: Comparison of efficiency of the prepared catalysts with some reported catalysts.

Scheme 1:



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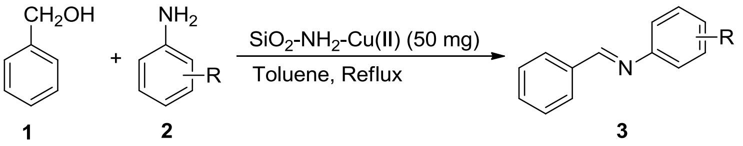

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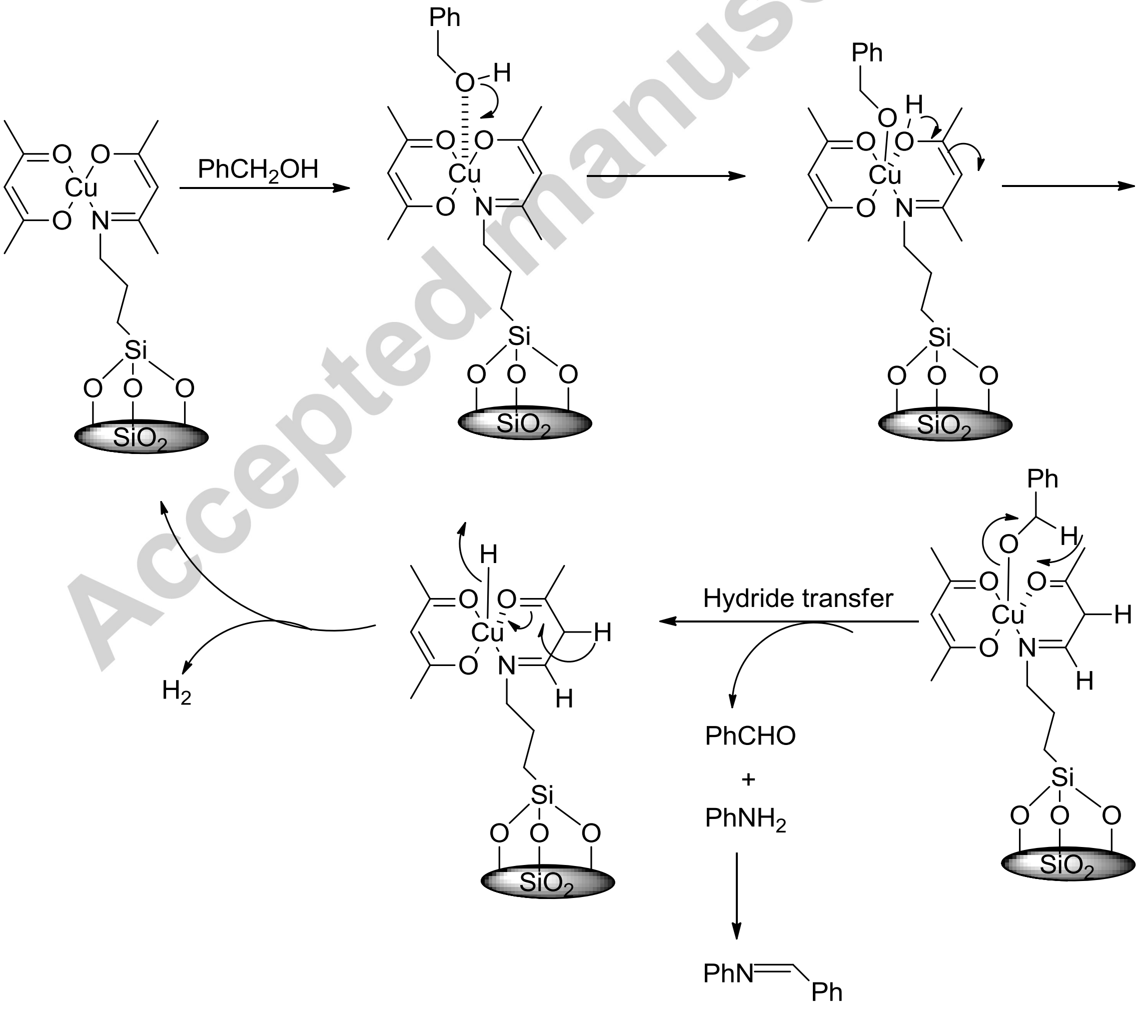

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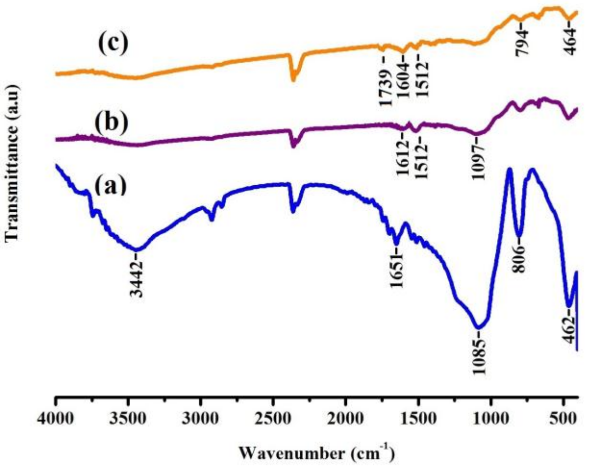

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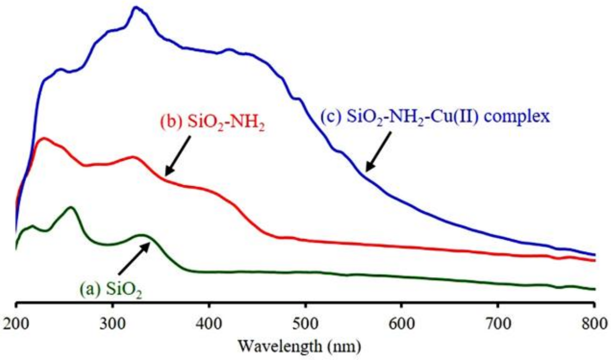

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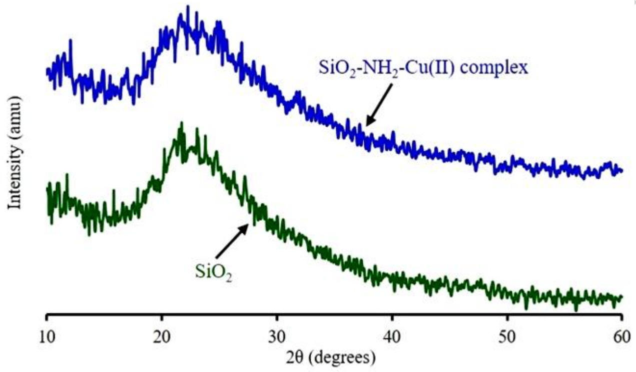

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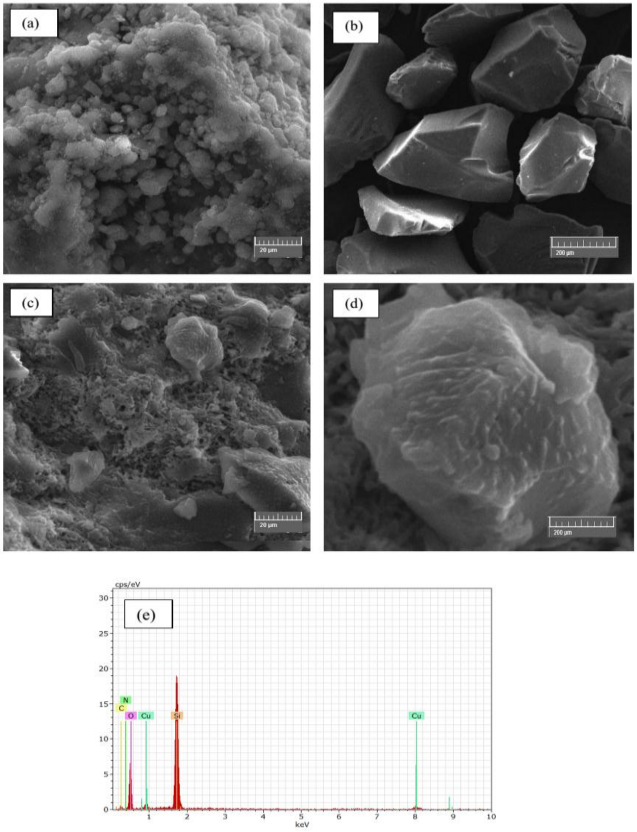
(a)
20 µm
(b)
200 µm
(c)
20 µm
(d)
200 µm
(e)
cps/eV
30
25
20
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10
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keV

Fig 5:

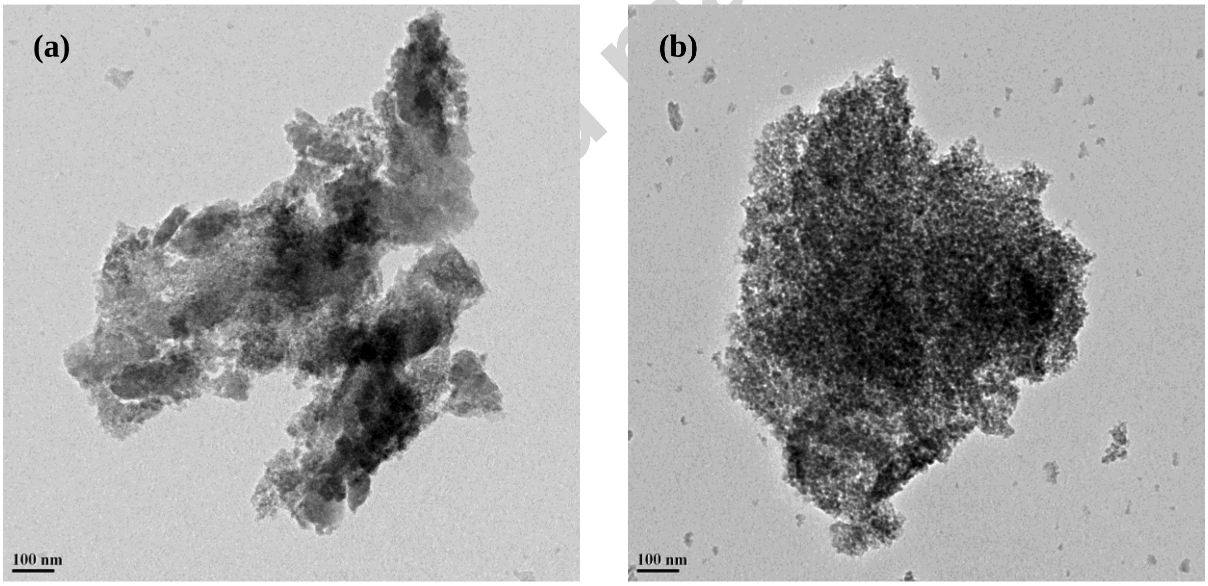
(a)
100 nm
(b)
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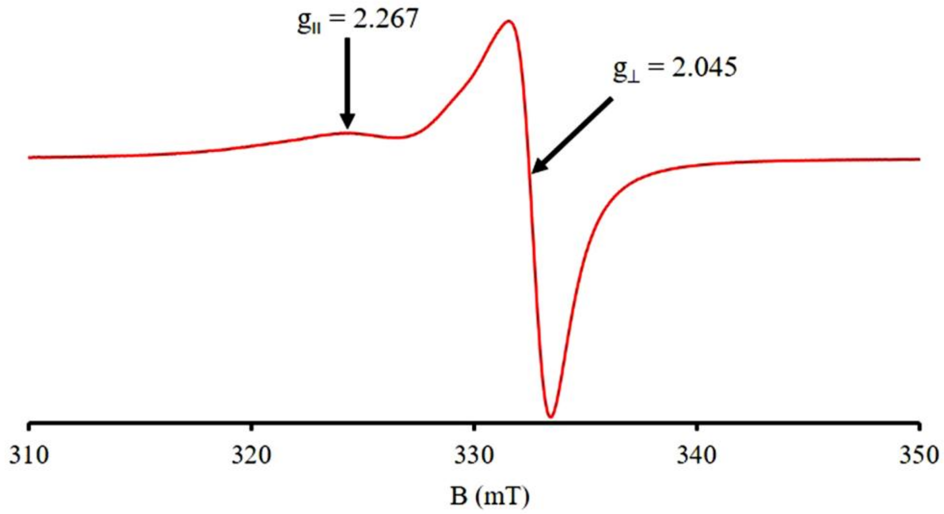
Fig 6:



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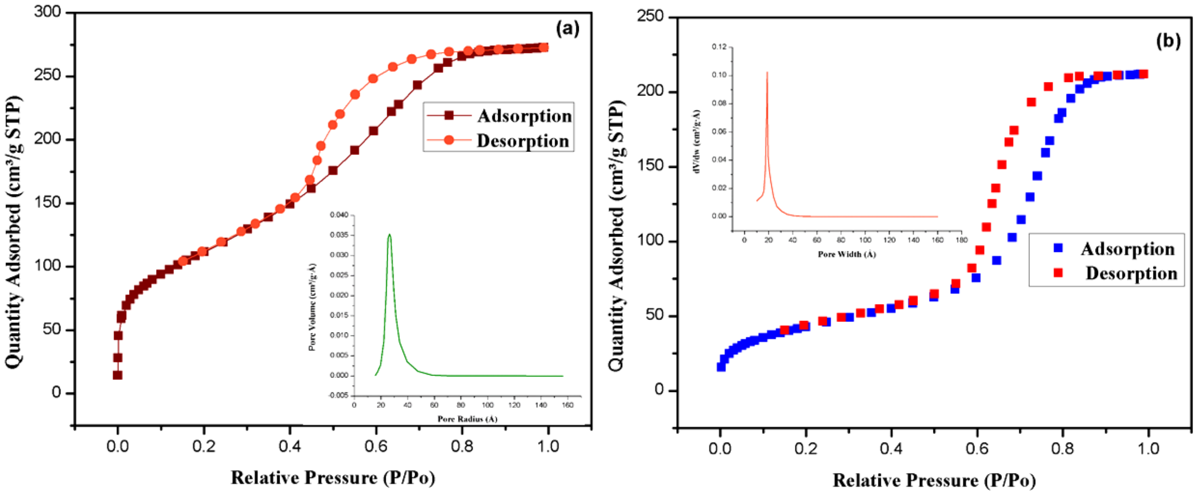


Table 1:

Entry	Solvent	Reaction time (h)	Yield (%)[c]	TON[d]	TOF[e](h^{-1})
1	Toluene[b]	24	-	-	-
2	Ethanol	24	55	147	6
3	Methanol	24	63	168	7
4	Dichloromethane	24	45	120	5
5	Toluene	10	94	251	25
6	Chlorobenzene	14	79	211	15
7	Nitrobenzene	18	73	195	11
8	Acetonitrile	12	81	216	18

[a] Oxidative condensation reaction of aromatic amines (1 equiv) with benzyl alcohol (1.5 equiv) using SiO_2-NH_2-Cu(II) Schiff base complex (50 mg, 0.375% Cu) in different solvents (10 ml) under refluxing conditions.

[b] Reaction carried out under neat conditions (without catalyst)

[c] Isolated yield.

[d] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.

[e] TOF = TON/time

Table 2:

Entry	Catalyst amount (mg, mol%)	Temperature (°C)	Reaction time (h)	Yield (%)[a]	TON[b]	TOF[c](h^{-1})
1	-	Reflux	24	-	-	-
2	10, 0.075	Reflux	20	21	280	14
3	20, 0.15	Reflux	18	30	200	11
4	30, 0.225	Reflux	15	64	284	19
5	40, 0.3	Reflux	12	72	240	20
6	50, 0.375	Reflux	10	94	251	25
7	100, 0.75	Reflux	10	94	125	12
8	50, 0.375	RT	24	18	48	2
9	50, 0.375	50	20	45	120	6
10	50, 0.375	80	13	80	213	16

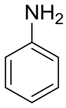
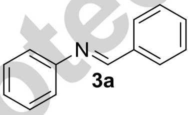
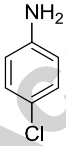
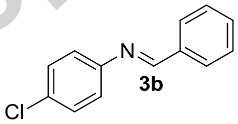
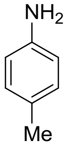
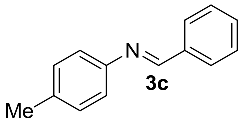
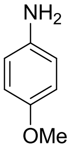
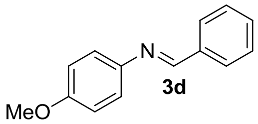
Oxidative condensation reaction of aromatic amines (1 equiv) with benzyl alcohol (1.5 equiv) using SiO_2-NH_2-Cu(II) Schiff base complex (50 mg, 0.375% Cu) in different temperature under refluxing toluene.

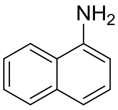
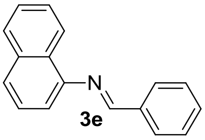
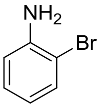
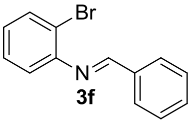
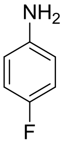
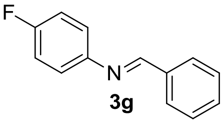
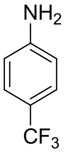
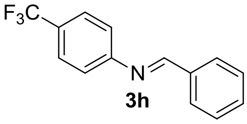
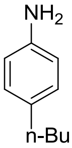
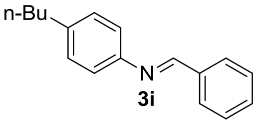
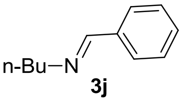
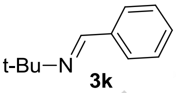
[a] Isolated yield.

[b] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.

[c] TOF = TON/time

Table 3:

Entry	Amine	Product (3(a-k))[b]	Time (h)	Yield (%)[c]	TON[d]	TOF[e](h^{-1})
1		 3a	10	94	251	25
2		 3b	9	92	245	27
3		 3c	8	96	256	32
4		 3d	8	95	253	32

5		 **3e**	10	75	200	20
6		 **3f**	11	78	208	19
7		 **3g**	10	91	245	24
8		 **3h**	15	73	195	13
9		 **3i**	8	92	245	31
10	n-Bu−NH$_2$	 **3j**	16	83	221	14
11	t-Bu−NH$_2$	 **3k**	14	89	237	17

[a] Oxidative condensation reaction of aromatic amines (1 equiv) with benzyl alcohol (1.5 equiv) using SiO_2-NH_2-Cu(II) Schiff base complex (50 mg, 0.375% Cu) in toluene (10 ml) under refluxing condition.

[b] All the compounds are known compounds and physical and spectral data are good agreement with literature.

[c] Isolated yield.

[d] Turnover number (TON) = (mmol of product)/(mmol of catalyst) after time t.

[e] TOF = TON/time

Table 4:

Cycle	Fresh	1	2	3	4	5
Yield (%)[b]	94	94	93	92	90	88

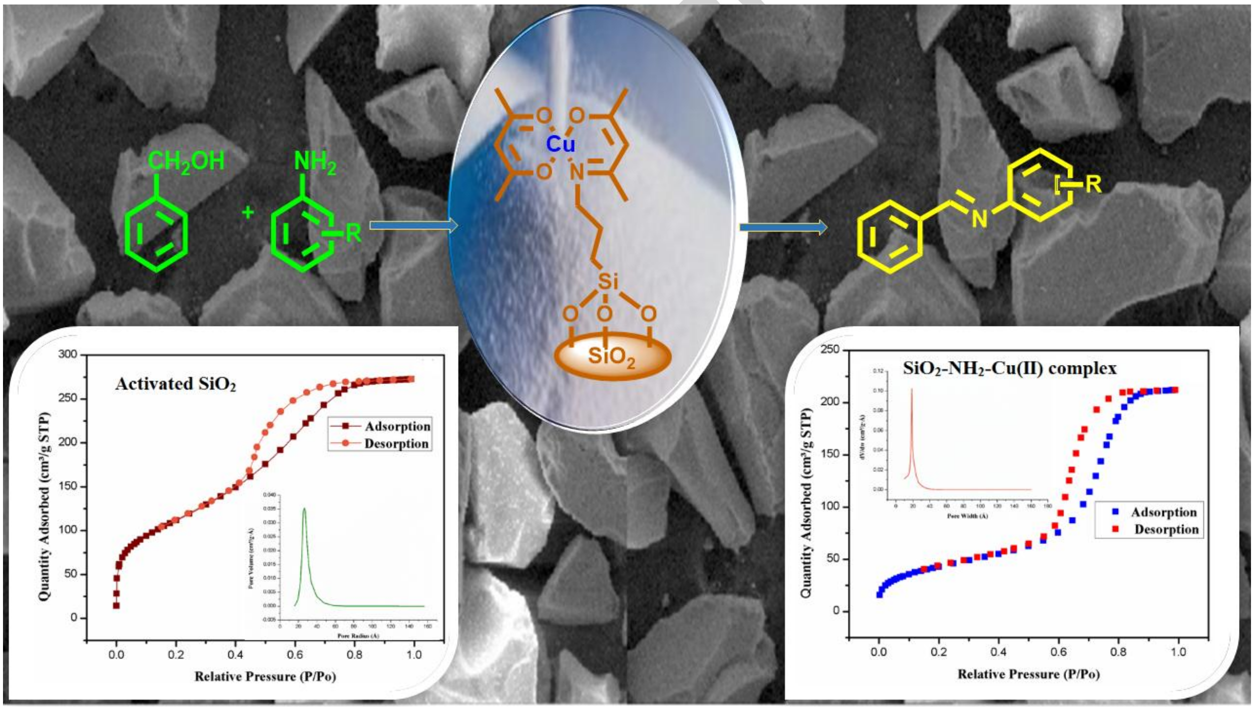
[a] Oxidative condensation reaction of aromatic amines (1 equiv) with benzyl alcohol (1.5 equiv) using SiO_2-NH_2-Cu(II) Schiff base complex (50 mg) in different solvents (10 ml) under refluxing conditions.

[b] Isolated yield.

Table 5:

Entry	Catalyst	Condition	Time (h)	Yield (%)	Reference
1	Pd/DNA $LiOH.H_2O$	H_2O, N_2 balloon, 50 °C	12	96[a]	[37]
2	$Cu(ClO_4)_2.H_2O$ (5 mol%)	KOH, Toluene, 70 °C O_2 balloon	19	97[b]	[38]
3	KOH	Air, Toluene, 90 °C	20	92[b]	[39]
4	Pd/AlO(OH) (4 mol%)	1 atm O_2, heptane 90 °C	20	90[b]	[40]
5	CeO_2 (50 mg)	Mesitylene (1.5 g) 60 °C, 24 h, air	24	93[c]	[41]
6	SiO_2-NH_2-Cu(II) (50 mg)	Toluene, Reflux	10	94[c]	This work

[a] Determined by GC-MS.
[b] Yields were determined by ^1H NMR.
[c] Isolated yield.



Highlights

- We successfully synthesized the silica functionalized Cu(II) Schiff base complex.
- The immobilization of the Cu(II) Schiff base complex on the surface of the silica material was confirmed by various physicochemical studies.
- The catalytic activity of the synthesized material was studied through the oxidative condensation reaction of benzyl alcohol with aromatic amines.
- Operational simplicity, activity under mild reaction conditions, excellent product yields with greater substrate scope are the advantages of this methods