

# Silica functionalized Cu(II) catalysed selective oxidation of benzyl alcohols using TEMPO and molecular oxygen as an oxidant

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**Abstract.** A general scheme for the oxidation of benzyl alcohols catalyzed by silica functionalized copper (II) has been designed. TEMPO, a free radical, assists this oxidation that was initiated by molecular oxygen which converts it to a primary oxidant. This catalytic combination i.e. SiO<sub>2</sub>-Cu(II) in presence of TEMPO and oxygen provides excellent results in terms of yields and reaction time. SiO<sub>2</sub>-Cu(II) was very well characterized by different spectroscopic techniques such as FTIR, XRD, TGA, XPS, EDAX, SEM, TEM and AAS and is recyclable upto five times which makes it economically beneficial.

**Keywords.** Oxidation; copper(II); aminopropyl silica; recyclability; TEMPO; molecular oxygen.

## 1. Introduction

The selective and catalytic oxidation of benzyl alcohols is a decisive functional group transformation in modern organic synthesis and in industrial processes. The significance of this reaction lies in the fact that aldehydes are the important key intermediates for the synthesis of other organic compounds in pharmaceuticals.<sup>1</sup> The aldehydes are also important moieties in plastic additives; processing of perfume and flavouring compounds and for the preparation of aniline dyes in the textile industry.<sup>2</sup> In earlier times, oxidation of alcohols has been carried out using stoichiometric amounts of chromium (VI) and manganese (VII)<sup>3,4</sup> but these methodologies require costly and toxic solvents.<sup>5</sup> and produced large amount of heavy metal wastes<sup>6</sup> thus making these methods highly undesirable. In this regard, non-waste producing oxidants like air, oxygen, hydrogen peroxide are more appealing as they are environmental friendly and cheap but these oxidants need to be activated by some cocatalyst.<sup>7</sup> Several catalytic systems using transition metal complexes and terminal oxidants are well known.<sup>8</sup> The use of persistent (TEMPO– 2,2,6,6-tetramethylpiperidinyl-1-oxyl, and its derivatives) or non-persistent (PINO– phthalimide-N-oxyl) nitroxyl radicals in oxidation reactions proves to be a better solution for various transition metal catalytic systems.<sup>9</sup> Copper as a catalyst is highly selective (which is the key feature of the reaction) and the uses of copper catalytic systems for this organic transformation are very well known.<sup>10</sup> But the use of these systems for oxidation of alcohols require large reaction times, use of toxic

oxidants and solvents, low yields of products, use of strong bases, less tolerance of functional groups, etc. Keeping in view of the above said disadvantages of other copper catalytic systems, we have extended our study for the oxidation capability of silica functionalized copper (II) catalyst towards the TEMPO mediated selective oxidation of benzyl alcohols using oxygen as an oxidant. This catalytic system i.e. SiO<sub>2</sub>-Cu(II)/TEMPO/O<sub>2</sub> proves to be very efficient for the selective synthesis of aldehydes from benzyl alcohols.

In this research work, we have used silica functionalized copper (II) for the aerobic oxidation of benzyl alcohols using TEMPO as a co-catalyst.

## 2. Experimental

### 2.1 Materials and Methods

Silica gel was purchased from ACROSS Organics and 3-aminopropyl(trimethoxy) silane and salicylaldehyde were purchased from Sigma Aldrich and were used without further purification. IR spectra of the catalyst and the synthesized compounds were recorded in the range of 4,000–300 cm<sup>-1</sup> on a Shimadzu Prestige-21 spectrophotometer. TGA of the catalyst was obtained on a Liness Thermal Analyser. X-ray diffractograms were recorded in 2 h range of 10–80 on a Panalyticals X'pert Pro X-ray diffraction spectrometer using CuK $\alpha$  radiation. XPS spectra of the catalyst were recorded on KRATOS ESCA model AXIS 165 (Resolution). SEM was recorded on JSM-7600F and TEM was recorded on Hitachi (H-7500) 120 kV with CCD camera. The atomic

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absorption spectrometric analysis (AAS) was done on Avanta-M atomic absorption spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of the compounds were obtained on Bruker Avance III (400 MHz) spectrometer. Mass spectra of the products were obtained on a Bruker Daltonics Esquire 3000 spectrometer.

## 2.2 General procedure for the oxidation of benzyl alcohols mediated by TEMPO and molecular oxygen

To a stirred solution of benzyl alcohol (0.5 mmol) in dry toluene, TEMPO (0.5 mmol), potassium carbonate (1.5 mmol) and silica functionalized copper (II) catalyst (0.2 g) was added. The reaction mixture was stirred at  $110^\circ\text{C}$  in an atmosphere of oxygen and monitored through TLC. When the reaction got completed, the reaction mixture was cooled to room temperature and was filtered. The residue was washed with water followed by EtOAc ( $3 \times 10$  mL). The filtrate was washed with brine solution and finally the product was obtained after the removal of solvent under reduced pressure followed by passing through column of silica and elution with EtOAc: pet ether (1:100).

## 3. Results and Discussion

### 3.1 Preparation and characterization of $\text{SiO}_2\text{-Cu(II)}$

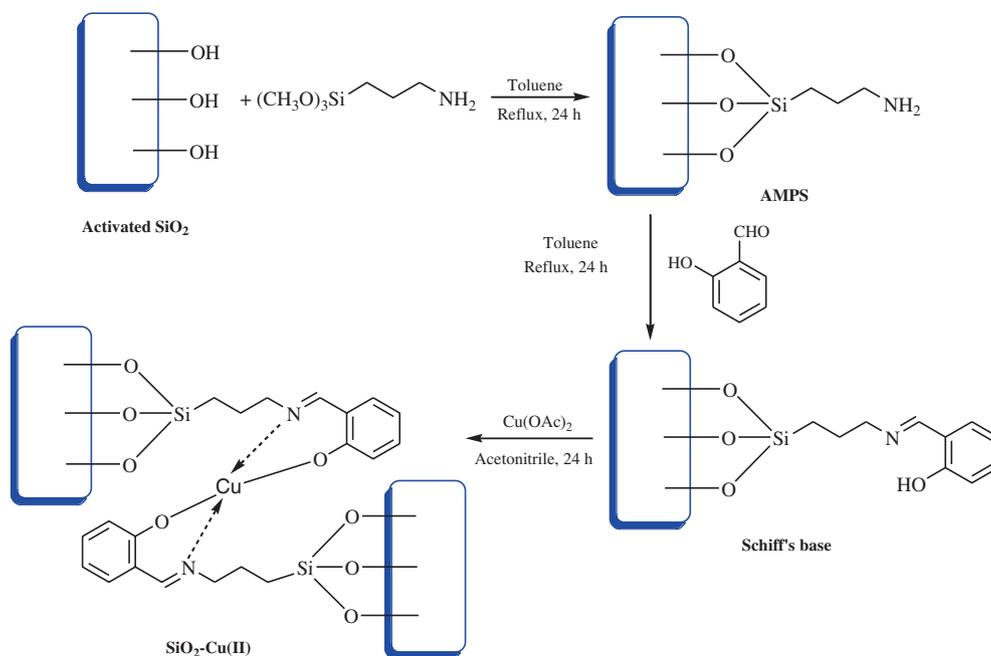
Silica functionalized copper (II) catalyst was prepared by the coordination of copper (II) acetate to salicyldimine to form a salen complex according to earlier reported procedure.<sup>11</sup>

This procedure involves the addition of activated silica to a solution of 3-aminopropyl(trimethoxy) silane in dry toluene and refluxed for 24 h to form 3-aminopropyl silica (AMPS). The AMPS was filtered off and dried in oven for 7 h and was further ligated by salicyldehyde to form schiff's base. For this, 3-aminopropyl silica was added to a solution of salicyldehyde in sodium dried toluene at  $110^\circ\text{C}$ . The imine or schiff's base so formed was filtered and washed with xylene thoroughly to remove any physical compounds present on silica followed by drying in oven. Finally, the mixture of schiff's base and copper (II) acetate was stirred in acetonitrile at room temperature for 24 h to form  $\text{SiO}_2\text{-Cu(II)}$ . The conditioning of the catalyst was done in water, ethanol and toluene to remove any physically adsorbed salts. The general scheme of the synthesis of  $\text{SiO}_2\text{-Cu(II)}$  is outlined in scheme 1.

The complete characterization of silica functionalized copper (II) was done by FTIR, XRD, TGA, XPS, EDAX, SEM, TEM, AAS [see supporting information]. The results are compiled in the form of a table 1. For the surface topography and internal structure of the catalyst, SEM and TEM images gave useful results. SEM images determine the porosity and homogeneity of the catalyst whereas TEM micrographs confirm the uniform distribution of copper (II) particles and their mean diameter is 8 nm (figures 1 and 2).

### 3.2 Catalyst testing for the oxidation of benzyl alcohols in toluene at $110^\circ\text{C}$

To optimize the reaction conditions for the oxidation of benzyl alcohols, 4-chlorobenzyl alcohol was taken



**Scheme 1.** Synthesis of silica functionalized copper (II) [ $\text{SiO}_2\text{-Cu(II)}$ ].

**Table 1.** Complete characterization of SiO<sub>2</sub>-Cu(II).

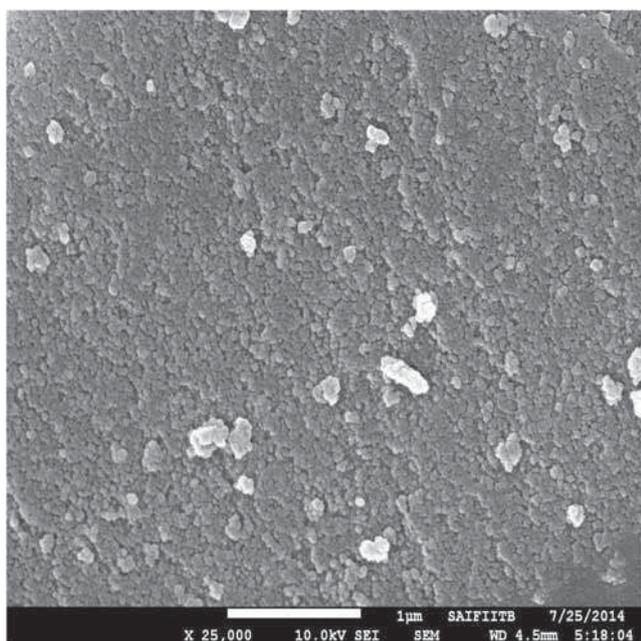
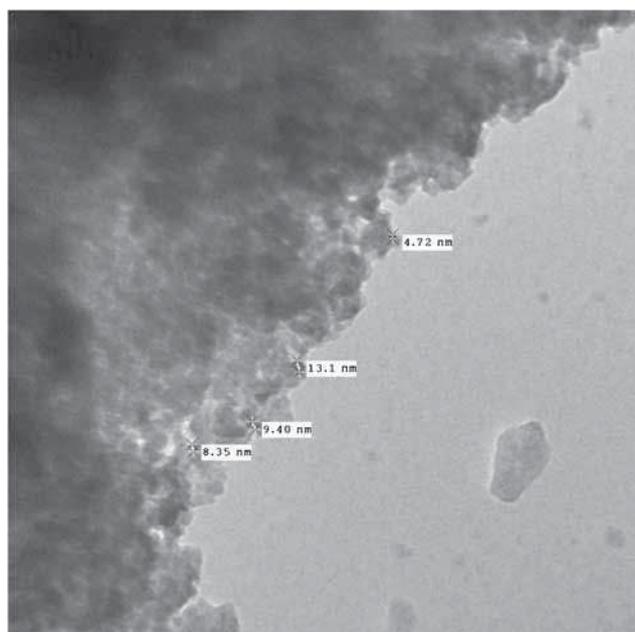
<i>Catalyst</i>	<i>Spectroscopic study</i>	<i>Description</i>
Silica functionalized copper (II) [SiO <sub>2</sub> -Cu(II)]	FTIR	3-aminopropylsilica displays CH <sub>2</sub> stretching bands at 2932 and 2863 cm <sup>-1</sup> . The FTIR of imine shows a sharp peak at 1632 cm <sup>-1</sup> due to C=N bond, which on complexation with copper disappears and appear as a band at 1625 cm <sup>-1</sup>
	TGA	Weight losses At 100°C, -1.75% due to loss of residual water 200°C, -4% 250°C, -10.5% <b>It is safe upto 225%.</b>
	XPS	A strong peak at 932.54 eV by Cu2p <sub>3/2</sub> photoelectrons.
	EDAX	The spectrum revealed the presence of elements like C, N, O, Si and Cu.
	AAS	The catalyst contained 0.0144 g of copper per gram of catalyst.

as a test substrate. The reaction conditions were then tested for different reaction conditions like temperature, solvent, oxidant and molar ratios of the catalyst. First of all, the reaction was performed at different temperatures and was found that 110°C was the suitable temperature to carry out the reaction successfully. No further increase in the yields of products were observed when the temperature rises beyond 110°C. The results are compiled in table 2.

After carrying out a series of reactions, it was found that 5 mol% of SiO<sub>2</sub>-Cu(II) is sufficient for the completion of the reaction. For choosing the appropriate solvent for oxidation of benzyl alcohols, different solvents were tried with the test substrate using SiO<sub>2</sub>-Cu(II) as

the catalyst (table 3). It was inferred from the table that toluene proved to be the best solvent in the reaction from all the solvents tested.

When oxidation of test substrate i.e., 4-chlorobenzyl alcohol was carried out in presence of potassium carbonate and SiO<sub>2</sub>-Cu(II) as a catalyst under open or oxygen atmosphere, the reaction proceeds to about only 45%. Further, addition of TEMPO, an oxidant increases the yield up to 55%. But, when the oxidation of 4-chlorobenzyl alcohol was done in presence of base, with TEMPO and molecular oxygen using SiO<sub>2</sub>-Cu(II) as the catalyst, the yield of the products surprisingly increased to 91%. The effect of oxidant is shown in figure 3.

**Figure 1.** SEM image of SiO<sub>2</sub>-Cu(II).**Figure 2.** TEM image of SiO<sub>2</sub>-Cu(II).

**Table 2.** Effect of temperature on the oxidation of benzyl alcohols catalyzed by SiO<sub>2</sub>-Cu(II)<sup>a</sup>.

Sl. No.	TEMPERATURE	TIME	YIELD <sup>b</sup>
1	30	3	35
2	60	3	55
3	80	3	76
4	100	3	88
5	110	3	91

<sup>a</sup>**Optimized reaction conditions:** 4-chlorobenzyl alcohol (0.5 mmol), TEMPO (0.5 mmol), potassium carbonate (1.5 mmol), SiO<sub>2</sub>-Cu(II) (0.2 g) and toluene (5 mL) under oxygen atmosphere.

<sup>b</sup>Yields based on separation through column chromatography

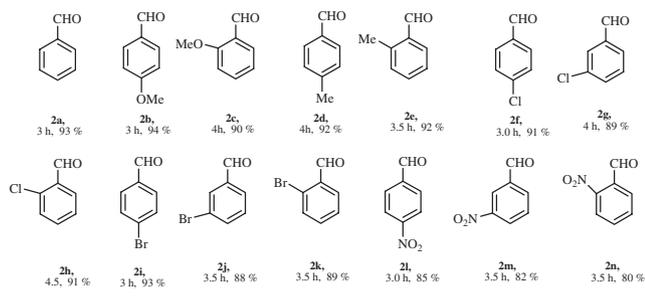
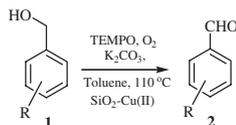
**Table 3.** Effect of solvent on the oxidation of benzyl alcohols catalyzed by SiO<sub>2</sub>-Cu(II).

Sl. No.	SOLVENTS	TIME	YIELD
1	Ethanol	3	64
2	Methanol	3	62
3	Acetonitrile	3	55
4	<b>Toluene</b>	<b>3</b>	<b>91</b>
5	Water	3	40

<sup>a</sup>**Optimized reaction conditions:** 4-chlorobenzyl alcohol (0.5 mmol), TEMPO (0.5 mmol), potassium carbonate (1.5 mmol), SiO<sub>2</sub>-Cu(II) (0.2 g) and solvent (5 mL) at 110°C under oxygen atmosphere.

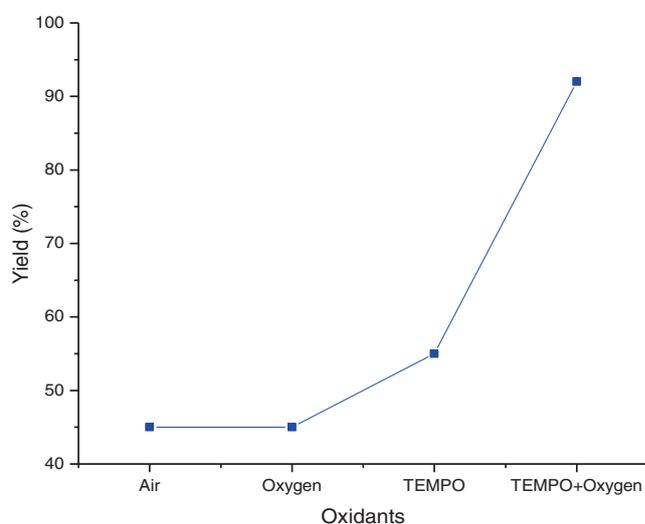
<sup>b</sup>Yields based on separation through column chromatography

To test the generality of the developed protocol, the reactions using different substrates with electron donating and electron releasing groups were investigated.



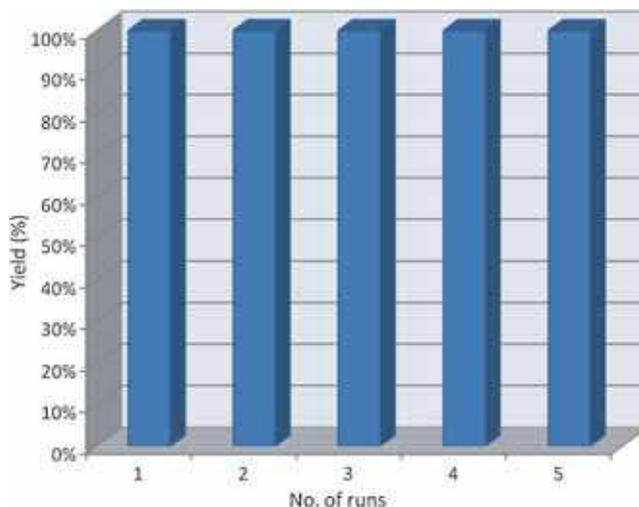
<sup>a</sup>**Optimized reaction conditions:** benzyl alcohol (0.5 mmol), TEMPO (0.5 mmol), potassium carbonate (1.5 mmol), SiO<sub>2</sub>-Cu(II) (0.2 g) and toluene (5 mL) at 110°C under oxygen atmosphere.

<sup>b</sup>Yields based on separation through column chromatography

**Figure 3.** Role of oxidants for the oxidation of benzyl alcohol catalyzed by SiO<sub>2</sub>-Cu(II).

<sup>a</sup>**Optimized reaction conditions:** 4-chlorobenzyl alcohol (0.5 mmol), potassium carbonate (1.5 mmol), oxidant, SiO<sub>2</sub>-Cu(II) (0.2 g) and toluene (5 mL).

<sup>b</sup>Yields based on separation through column chromatography

**Figure 4.** Recyclability graph of SiO<sub>2</sub>-Cu(II).

### 3.3 Recyclability test

In order to categorize silica functionalized copper (II) as heterogeneous catalyst, recyclability runs with the catalyst and test substrates under the optimized reaction conditions were needed to be done. It has been seen that the catalyst is recyclable up to fifth run without any appreciable loss in the activity which reflects the economical nature and greener aspect of the catalyst (figure 4).

## 4. Conclusions

In summary, we have explored the applications of silica functionalized copper (II) for the oxidation of benzyl

alcohols. It has been observed that the activity of the catalyst in combination with TEMPO and oxygen enhanced for the reaction and moreover, the reaction was very selective to aldehydes exclusively. Further, the economical nature of the heterogeneous catalyst was confirmed through the recyclability test. The catalyst was recyclable up to fifth use without any significant loss in the activity.

### Supplementary Information

Characterization of SiO<sub>2</sub>-Cu(II) and spectral details of all the compounds (3a-3n). Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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### References

- Figiel P J, Leskel M and Repo T 2007 *Adv. Synth. Catal.* **349** 11731
- (a) Musawir M, Davey P N, Kelly G and Kozhevnikov I V 2003 *Chem. Commun.* 1414; (b) Mallat T and Baiker A 1994 *Catal. Today* **19** 247
- Cainelli G and Cardillo G 1984 In *Chromium oxidants in organic chemistry* K Hafner (ed.) (Berlin: Springer-Verlag)
- Menger F M and Lee C 1981 *Tetrahedron Lett.* **22** 1655
- Rothenberg G, Feldberg L, Wiener H and Sasson Y 1998 *J. Chem. Soc. Perkin Trans.* **2** 2429
- March J 1992 In *Advanced Organic Chemistry S* Thomas (ed.) (New York: John Wiley) p. 1167
- (a) Arends I W C E and Sheldon R A 2004 In *Modern Oxidation Methods* J -E. Backvall (ed.) (New York: John Wiley) p. 83; (b) Skibida I P and Sakharow A M 1996 *Catal. Today* **27** 187; (c) Noyori R, Aoki M and Sato K 2003 *Chem. Commun.* 1977
- (a) Miyata A, Murakami M, Irie R and Katsuki T 2001 *Tetrahedron Lett.* **42** 7067; (b) Lee M and Chang S 2000 *Tetrahedron Lett.* **41** 7507; (c) Kakiuchi N, Maeda Y, Nishimura T and Uemura S 2001 *J. Org. Chem.* **66** 6620; (d) Steinhoff B A, Fix S R and Stahl S S 2002 *J. Am. Chem. Soc.* **124** 766 and references therein
- (a) Sheldon R A and Arends I W C E 2006 *J. Mol. Cat. A: Chemical* **251** 200; (b) Sheldon R A and Arends I W C E 2004 *Adv. Synth. Catal.* **346** 1051; (c) Ishii Y, Sakaguchi S and Iwahama T 2001 *Adv. Synth. Catal.* **343** 393; (d) Adam W, Saha-Müller C R and Ganeshpure P A 2001 *Chem. Rev.* **101** 3499; (e) Figiel P J, Sobczak J M and Polish 2001 *J. Chem.* **75** 869; (f) Liu R, Liang X, Dong C and Hu X 2004 *J. Am. Chem. Soc.* **126** 4112; (g) Velusamy S, Srinivasan A and Punniyamurthy T 2006 *Tetrahedron Lett.* **47** 923; (h) Figiel P J, Sobczak J M and Ziłkowski J J 2004 *Chem. Commun.* 244; (i) Minisci F, Recupero F, Cecchetto A, Gambarotti C, Punta C, Faletti R, Paganelli R and Pedulli G F 2004 *Eur. J. Org. Chem.* 109; (j) Minisci F, Punta C and Recupero F 2006 *J. Mol. Cat. A: Chemical* **251** 129
- Alizadeh M, Farzaneh F and Ghandi M 2003 *J. Mol. Catal. A: Chemical* **194** 283
- Gupta M, Gupta M, Kant R and Gupta V K 2015 *New J. Chem.* **39** 3578