RESEARCH ARTICLE

Applied Organometallic Chemistry

Bio-derived nanosilica-anchored Cu(II)-organoselenium complex as an efficient retrievable catalyst for alcohol oxidation

Rajjyoti Gogoi 💿 | Geetika Borah 💿

Department of Chemistry, Dibrugarh University, Dibrugarh, India

Correspondence

Geetika Borah, Department of Chemistry, Dibrugarh University, Dibrugarh, India. Email: geetikaborah@dibru.ac.in

Funding information UGC, New Delhi, India

Abstract

A new copper(II) complex supported onto rice-husk-derived nanosilica was prepared from 2,6-bis((phenylselanyl)methyl)pyridine, salicylaldehyde and copper acetate monohydrate, Cu(OAc)₂·H₂O. The as-synthesized complex Cu(II)SeNSe@imine-nanoSiO₂ (**Complex I**) was extensively characterized with FT-IR, powder XRD, SEM-EDX, solid-state UV-Vis, ESR, XPS, TGA and BET surface area analysis. The catalytic activity of the complex was explored for alcohol oxidation reactions using H_2O_2 as oxidant and acetonitrile as solvent. For comparison, we have also prepared an analogous homogeneous catalyst (**Complex II**) and characterized it with FT-IR, UV-Vis, LC-MS and ESR analyses. Its catalytic activity was also screened to the same reaction. The immobilized catalyst showed better efficiency with 75%–95% isolated yield compared with the homogeneous one for alcohol oxidation with at least five times recyclability without profound loss in activity.

Highlights

- 1. This is the first report of immobilized copper complex with Se–N–Se pincer ligand. Moreover, we have used bio-derived nanosilica as a solid support.
- 2. The alcohols are oxidized under environmentally benign mild reaction conditions using hydrogen peroxide as an oxidant.
- 3. The catalytic performance of the supported complex was compared with an analogous unsupported complex.

K E Y W O R D S

2,6-bis((phenylselanyl)methyl)pyridine, Cu(II) organoselenium, nanosilica, oxidation, rice-husk

1 | INTRODUCTION

The oxidation of alcohols to the corresponding carbonyl compounds is a highly relevant reaction in organic chemistry and is a fundamental and pivotal transformation in the synthesis of fine/bulk chemicals and pharmaceuticals.^[1,2] Till date, numerous methodologies

are available to affect this transformation.^[3–7] Traditionally, for the oxidation of alcohols to produce corresponding aldehydes/ketones, transition metals such as Cr(VI) and Mn(II) were widely used, which are toxic, corrosive and expensive.^[8–11] Moreover, several reports are available, which used Cr-, Mn-, Fe-, Cu-, Mo-, Ru-, Pt-, Pd-, Mn- and Os-based catalyst in the presence of

oxidants, such as molecular oxygen, tertiary butyl hydroxide (TBHP), hydrogen peroxide and sodium hypochlorite with toxic and costly solvents.^[8,12-18] In the last two decades, some desirable and efficient catalytic systems based on main group elements and ions, transition metal complexes and organometallic compounds had been developed and were performed exclusively in aqueous medium. However, copper had been extensively used in homogeneous catalysis for the aerobic oxidation of alcohols in water using Cu/TEMPO catalytic system. Substrate scope for aliphatic alcohols using water-based catalytic systems still poses a major challenge due to poor water solubility of the substrates.^[7] A triphasic system (solid-liquid-liquid) without co-solvent over microporous titanium silicate showed enhanced catalytic activity and para selectivity in the oxidation of benzyl alcohol, cyclohexanol, etc. compared with biphasic (solid-liquid) systems.^[19] In contemporary time, heterogenization of homogeneous system has received considerable attention due to distinct advantages of heterogeneous systems over homogeneous one, namely, relatively long lifetime of catalyst, easy separability, robustness and recyclability, and these factors form the crucial aspect of sustainability.^[2,20–26] This is why designing novel heterogeneous transition metal-based catalysts able to selectively oxidize alcohols in eco-friendly conditions is a continuously growing topic. In the last decade, a lot of papers had been published reporting the use of O_2 as the oxidizing agent and water as solvent; however, a few Cu, Au, Co and bimetallic catalysts were able to efficiently work with these greener conditions. Some examples where the use of ionic liquids as solvent allowed to achieve better results than with common organic solvents had also been reported for Cu, Pd, Fe and Co catalysts. Looking at the substrate scope, aliphatic alcohols still present the major challenge, except few protocols based on Co, Au, Pd and bimetallic systems that demonstrated high yield and good selectivity towards such substrates. However, it is worthy to mention that the costs related to the use of precious metals to activate oxygen remain too high for the use of such reactions in industry. As a result, the research community is gradually moving towards designing of low-cost heterogeneous catalysts based on Cu, Fe and Co, which were almost unexplored in their heterogeneous fashion up to 2012.^[6] Bhaumik and coworkers have reported the synthesis of functionalized mesoporous silica supported copper(II) and nickel(II) catalysts as well as polymer-anchored copper(II) catalyst for liquid-phase oxidation of olefins and aromatic alcohols.^[27,28] Very recently, a microporous framework copper silicate and Cu(II)-MOF catalyst have been reported for mild liquid-phase and base-free aerobic oxidation of alcohols using H_2O_2 the benzylic as oxidant,

respectively.^[29,30] Significant advancements had been made to synthesize immobilized copper nanoparticles and complexes with various ligands such as Schiff bases and N-heterocyclic carbene using silica, zeolite, clay, charcoal, nanocellulose, etc. as solid support, and their catalytic activity was investigated for alcohol oxidation and other transformations as well. As per our knowledge, there is not a single report of immobilized copper complex with Se-N-Se pincer ligand and investigation of its catalytic activity. Moreover, considering some specific characteristics like low cost, natural abundance, high surface area and high thermal stability, we have used rice-husk-derived nanosilica as solid support. Rice husk contains 90%-97% silica, the surface of silica contains silanol (Si-OH), and siloxane (Si-O-Si) groups are responsible for binding with other functional groups.^[31] From the view point of using low-cost metal and agro-waste-derived nanosilica as base material and in continuation of our preceding work as well, the authors report the development of rice-husk-derived nanosilicaanchored Cu(II)-Se-N-Se complex and evaluation of its catalytic activity towards oxidation of primary and secondary alcohols to their corresponding carbonyl compounds.^[8]

2 | EXPERIMENTAL

2.1 | Materials

All chemicals were of AnalaR grade and obtained commercially. They were used as received without further drying or purification. Solvents such as ethanol, methanol, dimethyl sulfoxide, acetonitrile, ethyl acetate, toluene, chloroform and oxidant $H_2O_2(30\%)$ were purchased from Merck. Copper(II) acetate monohydrate, diphenyl diselenide and 2,6-bis(bromomethyl)pyridine were purchased from Sigma-Aldrich. The alcohol substrates were purchased from Sigma-Aldrich and Tokyo Chemical Industry and were used as received without further treatment.

2.2 | Physical measurements

The powder x-ray diffraction (PXRD) patterns of silica and silica supported materials were recorded on Rigaku Ultima IV diffractometer using Cu-K α radiation ($\lambda = 1.541$ Å) at 40 kV and 30 mA. The Fourier transformed infrared (FT-IR) spectra were recorded as KBr pellets on a Shimadzu IRPrestige-21 FT-IR spectrophotometer (200–4000 cm⁻¹). The solid-state UV-visible (UV-Vis) spectra were obtained with a Jasco V-750 spectrometer in the wavelength range 200–800 nm. ESR spectra of the catalysts were recorded on JEOL JES-FA200 ESR spectrometer. The copper content of Complex I was determined by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis with an ARCOS simultaneous ICP spectrometer at SAIF, IIT Bombay. The atomic percentage of different elements in **Complex I** were evaluated from XPS survey spectrum using casaXPS software. The Brunauer-Emmett-Teller (BET) surface area of the materials at liauid nitrogen temperature was recorded on Quantachrome instrument (Boynton Beach, FL, 33426, USA). The SEM photographs of the as-prepared materials were performed on JEOL JSM IT-300 operating at 20 kV accelerating voltage. The EDX spectra were also recorded on the same instrument attached to the scanning electron microscope. X-ray photoelectron spectra (XPS) were recorded using XPS-AES Module, Model: PHI 5000 Versa Prob II. The C (1s) electron binding energy corresponding to graphitic carbon was used for calibration of the Cu (2p) and Se (3d) core-level binding energy. GC mass spectrograms of the products were obtained using Agilent Technologies GC system 7820 coupled with a mass detector 5975 and SHRXI-5MS column. ESI-MS spectrum of the complex was recorded in a Thermo Fisher Endura LC/MS mass spectrometer. HR-MS data were recorded by electron spray ionization with Q-TOF mass analyser.

2.3 | Synthesis of ligand (L₁) {2,6-bis ((phenylselanyl)methyl)pyridine}

A solution of diphenyl diselenide (Ph_2Se_2) (0.312 g, 1 mmol) in 30 ml of ethanol was stirred under N₂ atmosphere. Then, NaBH₄ (0.076 g, 2 mmol) dissolved in 5 ml of aqueous NaOH (5%) was added to it dropwise until the solution became colourless due to formation of PhSeNa. Thereafter, 2,6-bis(bromomethyl) pyridine (0.264 g, 1 mmol) dissolved in 10 ml of ethanol was added to the colourless solution with constant stirring for 3 h. While the resulting solution was poured into cold water (30 ml), a solid product was obtained, which was extracted with chloroform (4 × 25 ml) from the aqueous layer. The extract was washed with water $(3 \times 40 \text{ ml})$, followed by drying over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure on a rotary evaporator to result in a yellow viscous oil, which upon mixing with methanol (5 ml) and placing in a refrigerator (5°C) gave crystals of 2,6-bis((phenylselanyl)methyl)pyridine ligand (L₁) given in scheme 1. The ligand L₁ was characterized by FT-IR analysis and high-resolution mass spectroscopic (HR-MS) technique (Figures S1 and S2).^[14]

2.4 | Synthesis of Cu(II)SeNSe@iminenanoSiO₂ complex (Complex I)

The complex Cu(II)SeNSe@imine-nanoSiO₂ was prepared by a route given in Scheme 2. The nanosilica was extracted from paddy waste rice husk according to the literature report without modification.^[32] The procedure was mentioned in detail in the Supporting Information.

2.4.1 | Immobilization of APTES onto nanosilica

A 3.8 g nanosilica (dried overnight at 250° C) and aminopropyltriethoxysilane (APTES) (0.442 g, 2 mmol) were added to a dry toluene (100 ml), followed by refluxing for 6 h under N₂ atmosphere. After cooling the resulting mixture, a solid product formed. The solid product was separated by filtration, washed with dry toluene for several times through Soxhlet extraction and dried at 120° C for 24 h. The as-synthesized product was designated as APTES@nanoSiO₂.

2.4.2 | Synthesis of imine functionalized nanosilica

A 0.77 g of APTES@nanoSiO₂ was added to a 60-ml ethanol, followed by addition of salicylaldehyde (0.086 g, 0.707 mmol). The mixture was refluxed for 6 h with





Cu(II)SeNSe@imine-nanoSiO₂

SCHEME 2 Synthesis of Cu(II)SeNSe@imine-nanoSiO₂ (Complex I)

constant stirring. A yellow solid was formed, which was separated out and washed repeatedly through Soxhlet extraction with ethanol and acetone. The resulting mixture was dried at 120°C for 24 h and designated as imine@nanoSiO2.

2.4.3 | Immobilization of Cu(II) and 2,6-bis ((phenylselanyl)methyl)pyridine onto imine@nanoSiO₂

A 0.03 g (0.16 mmol) of (CH₃COO)₂Cu·H₂O was added to 10-ml acetone, followed by addition of 1 g imine $(\alpha$ nanoSiO₂ and 0.066 g (0.16 mmol) of 2,6-bis ((phenylselanyl)methyl)pyridine ligand. The mixture was refluxed for 24 h under N2 atmosphere. A browncoloured solid was formed, which was filtered off,

followed by washing with dry toluene through Soxhlet extraction and dried at 120°C for 24 h. The solid product was designated as Cu(II)SeNSe@imine-nanoSiO₂ (Scheme 2). The Cu content of the catalyst was found to be 0.18 mol% per10 mg from ICP-AES analysis.

2.4.4 | Synthesis of Cu(II)Se-N-Se-imine (Complex II)

A 0.127 g (0.64 mmol) of Cu(CH₃COO)₂·H₂O was dissolved in 50 ml of ethanol. To this solution, 0.266 g (0.64 mmol) N-benzylideneaniline Schiff base (pre-synthesized) and 0.121 g (0.64 mmol) 2,6-bis((phenylselanyl) methyl)pyridine ligand was added and allowed to stir for 6 h at 60°C (scheme 3). A reddish-brown-coloured solid was obtained, which was filtered off and washed with



SCHEME 3 Synthesis of Cu(II)Se-N-Se-imine (Complex II)

ethanol. Molecular weight was found to be 781 g/mol (Figure S3).

2.5 | General procedure for alcohol oxidation

A 0.010 g (0.18 mol% of Cu per 10 mg) of the catalyst Cu(II)SeNSe@imine-nanoSiO2 was charged to a roundbottom flask containing a mixture of alcohol (1 mmol), oxidant (0.3 ml) and solvent (4 ml). Reaction mixture was stirred at 80°C for the required time. The progress of the reaction was monitored by the thin-layer chromatography (TLC) method. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated out by centrifugal precipitation. The filtrate was extracted with water (10 ml) and ether $(3 \times 10 \text{ ml})$. The organic layer thus collected was washed with brine and dried over anhydrous Na₂SO₄, and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (mesh 60-120) using ethyl acetate and hexane mixture (2:8) as the eluent to obtain the desired product in pure form. The product was characterized by GC-MS and FT-IR analysis and compared with literature data.

While recycling the catalyst, after each cycle, it was isolated from the reaction mixture by simple centrifugation, washed with water and ethyl acetate for several times and dried in an oven at 120°C for overnight. The recovered catalyst was then subjected for next run under identical reaction conditions.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization of the materials

3.2 | X-ray diffraction study

XRD patterns of silica, nanosilica and the catalyst are demonstrated in Figure 1. The PXRD of silica (Figure 1a) exhibits peaks at 20 values of 19.05° , 20.36° , 24.75° , 28.83° , 29.25° , 32.45° , 38.12° , 49.33° , 55.34° and 59.60° corresponding to (100), (101), (102), (110), (111), (202), (202), (210), (211) and (220) planes of hexagonal unit cell.^[33] The sharp peaks of silica indicated its crystalline nature. The XRD pattern of nanosilica (Figure 1b) exhibits one broad peak in the range $20-23^{\circ}$, which can be ascribed to amorphous silica.^[34,35] The XRD pattern of



FIGURE 1 XRD patterns of (a) silica, (b) nanosilica and (c) Cu(II)SeNSe@iminenanoSiO₂ (**Complex I**)

Cu(II)SeNSe@imine-nanoSiO₂ (Figure 1c) shows 2 θ values at 15.0°, 24.7°, 25.0°, 29.02°, 30.7°, 36.4°, 47.01°, 52.7°, 59.64° and 65.17° corresponding to (100), (110), (111), (020), (210), (211), (221), (311), (222) and (322) planes of hexagonal Cu(II) system.^[36,37]

3.2.1 | FT-IR study

The FT-IR spectra of imine@nanoSiO₂ and Cu(II)SeN-Se@imine-nanoSiO₂ (**Complex I**) provided valuable information regarding bonding. The spectrum of imine@nanoSiO₂ showed a medium-intensity peak at 1644 cm⁻¹, attributed to C=N stretching vibration of -CH=N. However, this band was shifted to 1632 cm⁻¹ in the spectrum of Cu(II)SeNSe@imine-nanoSiO₂, substantiating involvement of azomethine-N to the coordination with Cu(II). The spectra of imine@nanoSiO₂ and Cu(II)SeNSe@imine-nanoSiO₂ and Cu(II)SeNSe@imine-nanoSiO₂ and Cu(II)SeNSe@imine-nanoSiO₂ (Figure 2b,c) demonstrated that a strong and broad peak at 1109 and

1101 cm⁻¹, respectively, could be assigned to the asymmetric stretching frequency of structural siloxane framework (Si–O–Si), whereas the band observed at 800 and 816 cm⁻¹ corresponded to symmetric stretching of the same group.^[38,39] The bending vibration of Si–O–Si showed peak at 476 cm⁻¹ for imine@nanoSiO₂; however, the bands are shifted slightly either higher or lower frequency compared with that of Cu(II)SeNSe@iminenanoSiO₂. The spectrum of imine@nanoSiO₂ showed ν (OH) vibration of phenolic –OH group at 3443 cm⁻¹, which was shifted to the region 3321–3645 cm⁻¹ in the complex, confirming non-participation of phenolic oxygen to the coordination with Cu(II).^[5,9]

The far-infrared (IR) spectrum of Cu(II)SeN-Se@imine-nanoSiO₂ showed peaks at 522 cm⁻¹ and 511 cm⁻¹, which could be assigned to asymmetric and symmetric stretching vibrations of C–Se bond (Figure 3).^[40] The broad and strong band at 469 cm⁻¹ might be attributed to the torsion vibration of rings, coupled with the C–Se bending vibrations.^[41] The

(c) Cu(II)SeNSe@imine-nanoSiO₂ (**Complex I**)



bending/torsional modes of Cu–N and Cu–O bonds may submerge with this broad band. Stretching vibrational frequencies of Cu–N and Cu–O bonds are observed at 565, 549 and 631 cm⁻¹.^[42,43] The bands at 362 cm⁻¹ and 392 cm⁻¹ could be assigned to stretching vibrations of Cu–Se bond.^[44]

The FT-IR spectrum of Cu(II)Se-N-Se-imine (**Complex II**) showed a strong intensity C=N stretching vibration of -CH=N group at 1609 cm⁻¹, whereas ν (C=O) and ν (C-O) of acetate group were observed at 1751 and 1381 cm⁻¹, respectively, with other expected peaks (Figure S4). The far-IR spectrum of Cu(II)Se-N-Se-imine (Figure 4) showed peaks at 526, 517 and 507 cm⁻¹, which could be assigned to asymmetric and symmetric stretching vibrations of C–Se bond.^[40] Different stretching

vibrational frequencies of Cu–N and Cu–O bonds were observed at 590, 582, 569, 569 and 545 cm⁻¹.^[42,43] The bands at 343, 331 and 317 cm⁻¹ could be assigned to stretching vibrations of Cu–Se bond.^[44]

3.2.2 | EPR study

The ESR spectrum of **Complex I** clearly showed parallel and perpendicular components of tetragonally distorted Cu(II) complex with average g_{\parallel} value at 2.42 and g_{\perp} at 2.02, respectively (Figure 5).^[45,46] The narrow hyperfine lines associated with perpendicular component clearly enumerate super-hyperfine coupling of unpaired electron spin of Cu(II) with the nuclear spin of nitrogen atoms



FIGURE 4 Far-FT-IR spectrum of Cu(II)Se-N-Se-imine (Complex II)

8 of 17



FIGURE 5 ESR spectrum of Cu(II)SeNSe@imine-nanoSiO₂ (Complex I)



FIGURE 6 ESR spectrum of Cu(II)Se-N-Se-imine (Complex II)

 $(I_{\rm N}=1)$, substantiating coordination through *N*-atoms. But the unsupported Complex II demonstrated only perpendicular component at 2.05 and could be attributed to the formation of tetragonally distorted complex (Figure 6).

3.2.3 | XPS study

XPS measurements have been carried out on Cu(II)SeN-Se@imine-nanoSiO₂ (**Complex I**) to ascertain the chemical state of Cu and Se in the catalyst (Figure 7). The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks at 933.1 and 952.2 eV, respectively, were characteristic of Cu(II). Additionally, the presence of Cu(II) could also be confirmed by the shakeup peak observed at ~945 eV.^[47,48] The XPS spectrum of complex showed characteristic peaks at 51.27 and 56.12 eV with a spin–orbit splitting of 4.85 eV, which could be attributed to Se $3d_{5/2}$ and $3d_{3/2}$ of metallic selenium, respectively.^[49] The full XPS survey spectrum of Cu(II)SeNSe@imine-nanoSiO₂ with atomic percentage has been incorporated in Figure S5.

3.2.4 | BET study

The BET surface areas of silica. nanosilica. APTES@nanoSiO₂ and Cu(II)SeNSe@imine-nanoSiO₂ are shown in Table 1. It has been observed that nanosilica has higher specific surface area than the silica as expected. The decrease of surface area for APTES@nanoSiO2 and Cu(II)SeNSe@imine-nanoSiO2 compared with nanosilica strongly affirmed the successful grafting of APTES, imine and the metal complex on the nanosilica.



FIGURE 7 High-resolution XPS spectra of (a) Cu 2p core level and (b) Se 3d for Cu(II)Se-N-Se@imine-nanoSiO₂ catalyst



3.2.5 | SEM-EDX study

SEM micrographs (Figure 8a,b) clearly indicated that the morphology of nanosilica was changed after successive immobilization of APTES, imine, ligands and Cu(II) onto the surface of nanosilica. The presence of copper, nitrogen and selenium along with the carbon, oxygen and

TABLE 1 BET surface area measurements of the silica- based materials

Entry	Materials	Surface area(m²/g)
1	Silica	186
2	Nanosilica	280
3	APTES@nanoSiO ₂	152
4	Cu(II)SeNSe@imine-nanoSiO ₂	123

silicon in the catalyst was confirmed from SEM-EDX analysis.

3.2.6 | TGA study

The imine ligand content was measured by TGA analysis. The TGA analysis of APTES@nanoSiO₂ (Figure S6) and imine@nanoSiO₂ (Figure S7) revealed an initial weight loss of approximately 5.80 and 7.11%, respectively, up to temperature $\sim 250^{\circ}$ C, which could attributed to adsorbed water and organic be With moiety. further increase in temperature, APTES@nanoSiO2 and imine@nanoSiO2 showed 4.75 and 4.05%wt. loss corresponding to the decomposition of APTES and APTES-imine, respectively. Thus, the quantity of imine ligand attached to the copper was measured from the TGA analysis and was found to be 0.61 wt% in the catalyst (Table 2). Complex I showed



(a)

(b)



FIGURE 8 (a) SEM image of nanosilica. (b) SEM image of Cu(II)SeNSe@imine-nanoSiO₂. (c) SEM-EDX of nanosilica. (d) SEM-EDX of Cu(II)SeNSe@imine-nanoSiO₂



TABLE 2 TGA-DTG analysis of the materials

Entry	Material	% weight loss (100–250°C)	% weight loss (250–550°C)	wt% ligand
1	APTES@nanoSiO ₂	5.80	4.05	
2	Imine@nanoSiO ₂	7.11	4.75	0.61%
3	Cu(II)SeNSe@imine-nanoSiO ₂	13.12		

TABLE 3 Optimization of reaction conditions for oxidation of 1-phenylethanol^a

		OH	Cu(II)SeNSe@imine-	nanoSiO ₂		
			solvent ,oxidant	CH3		
				· ·		
Entry	Solvent	Oxidant	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%) ^b
1	H ₂ O	H_2O_2	10	rt	180	-
2	H ₂ O	H_2O_2	10	50	180	40
3	C ₂ H ₅ OH	H_2O_2	10	rt	180	35
4	C ₂ H ₅ OH	H_2O_2	10	50	180	56
5	MeOH	H_2O_2	10	rt	180	20
6	MeOH	H_2O_2	10	50	180	45
7	MeOH (64.7 °C)	H_2O_2	10	rt	180	48
8	CH ₂ Cl ₂ (39.6)	H_2O_2	10	rt	180	35
9	THF (66)	H_2O_2	10	rt	180	45
10	Toluene	H_2O_2	10	80	180	62
11	CH ₃ CN(82)	H_2O_2	10	80	180	95
12	CH ₃ CN	H_2O_2	10	80	180	95 [°]
13	-	H_2O_2	10	80	180	Trace
14	CH ₃ CN	-	10	80	180	Trace
15	CH ₃ CN	H_2O_2	8	80	180	92
16	CH ₃ CN	H_2O_2	15	80	180	95
17	CH ₃ CN	H_2O_2	20	80	180	95
18	CH ₃ CN	H_2O_2	-	80	180	-
19	CH ₃ CN	Air	10	rt	24 h	-
20	CH ₃ CN	TBHP	10	rt	24 h	45
21	CH ₃ CN	H_2O_2	10	80	120	92
22	CH ₃ CN	H_2O_2	10	80	180	90 ^d
23	CH ₃ CN	H_2O_2	6	80	180	25 ^e
24	CH ₃ CN	H_2O_2	6	80	180	$31^{\rm f}$

^aReaction conditions: 1-phenyl ethanol (1 mmol, 0.062 ml), H_2O_2 (0.3 ml, 30%), TBHP (0.3 ml), solvent (4 ml), Cu(II)SeNSe@imine-nanoSiO_2 (8–20 mg; 0.144–0.36 mol% of Cu).

^bIsolated yield.

^cH₂O₂ (0.5 ml, 30%).

^dH₂O₂ (0.2 ml, 30%).

^eNanosilica as catalyst.

^fAPTES@nanoSiO₂ as catalyst.

12 of 17 WILEY Applied Organometallic Chemistry

TABLE 4 Oxidation of various alcohols to corresponding carbonyl compounds



TABLE 4 (Continued)



Note: Reaction conditions: substrate (1 mmol), H₂O₂ (0.3 ml, 4 mmol), CH₃CN (4 ml), Cu(II)SeNSe@imine-nanoSiO₂ (10 mg, 0.18 mol% of Cu). ^aIsolated yield.

a 13.12% weight loss in the temperature region 100–400° C (Figure S8).

3.2.7 | UV-Vis study

The solid-state UV-Vis spectra of 2,6-bis((phenylselanyl) methyl)pyridine, imine@nanoSiO₂ and Cu(II)SeN-Se@imine-nanoSiO₂ showed absorptions around 200–400 nm, which could be attributed to intraligand π – π * and n– π * electron transfer. The spectrum of Cu(II)SeN-Se@imine-nanoSiO₂ (**Complex I**) exhibited a weak broad peak at ~690 nm, which might be assigned to [2] $E_g \rightarrow {}^2T_{2g}$ transition of Cu²⁺ in a nearly octahedral environment (Figure S9). Identically, the analogous unsupported Complex II showed a characteristic band at 565 nm, attributed to [2] $E_g \rightarrow {}^2T_{2g}$ transition of Cu²⁺ in a nearly octahedral environment (Figure S9).

3.3 | Catalytic activity

After characterization, catalytic efficiency of the complex was explored for the oxidation of primary and secondary alcohol to their corresponding carbonyl compounds. Initially, to optimize the reaction conditions with respect to catalyst amount, solvent, oxidant, temperature, reaction time, etc., a set of reactions were performed taking 1-phenylethanol as a model substrate. We have screened various solvents such as H_2O , MeOH, C_2H_5OH CH_2Cl_2 , THF, toluene and CH_3CN and observed acetonitrile gave 95% product yield in 180 min (Table 3, Entry 11). But in solvent and oxidant-free conditions, the reaction produced a trace amount of product (Table 3, Entries 13 and 14).

We observed that increasing the amount of catalyst from 10 (0.18 mol% of Cu) to 20 mg (0.36 mol% of Cu)



TABLE 5 Oxidation of various alcohols to corresponding

Note: Reaction conditions: substrate (2 mmol), H_2O_2 (0.3 ml, 4 mmol), CH_3CN (4 ml), Cu(II)Se-N-Se-imine (**Complex II**) (6 mg, 5 mol%). ^aIsolated yield.

^bTime 24 h.

did not alter the product yield (Table 3, Entries 16 and 17), whereas decreasing the catalyst amount to 8 mg (0.144 mol% of Cu) decreased the yield (Table 3, Entry 15). However, the reaction did not proceed in the absence of the catalyst (Table 3, Entry 18). While applying nanosilica and APTES@nanoSiO₂ as catalyst, 25% and 31% product yields have been isolated, respectively (Table 3, Entries 23 and 24). The optimization of reaction temperature showed that at 80°C in acetonitrile, the alcohols were highly activated and gave excellent yield.

Using the optimized reaction conditions, a variety of structurally different alcohols have been tested for oxidation to corresponding carbonyl compounds. The results are summarized in Table 4. It is clear that both aromatic (primary and secondary) and aliphatic alcohols can be activated with this protocol. However, aromatic alcohols gave higher product yield compared with aliphatic alcohols in many cases.

3.4 | Catalyst leaching and reusability

3.4.1 | Hot filtration test

We have carried out the hot filtration test to investigate the heterogeneous nature of the catalyst and to make sure non-leaching of Cu during the course of catalytic reactions. To perform the test, a mixture of Cu(II)SeN-Se@imine-nanoSiO₂ (15 mg, 0.27 mol% of Cu), 1-phenylethanol (122 mg, 1 mmol), H_2O_2 (0.3 ml), H_2O (4 ml) and CH_3CN (4 ml) was stirred at 80°C. We have checked percentage conversions at 20-min time interval and found 22% and 42% conversions. After 1 h, the reaction was stopped and the catalyst was separated out from the hot reaction mixture. The product was identified by GC-MS (50% conversion). The reaction was allowed to continue with the filtrate without solid catalyst for another 2 h. The percentage conversion, as examined by GC, showed constancy at 50% even after 2 h (Figure S11). Moreover, the ICP-AES analysis of the filtrate showed that the content of Cu in the filtrate was less than the detection limit. These results affirmed the non-leaching process during the course of the catalytic reaction.

3.4.2 | Reusability

To check retrievability of the catalyst, the oxidation reaction was started taking 30 mg of the catalyst (0.54 mol% of Cu), 1-phenylethanol (1 mmol), H_2O_2 as oxidant (0.3 ml) and solvent (4 ml) using optimized reaction conditions. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugal precipitation, followed by washing thoroughly with acetonitrile–water mixture. Recovered catalyst was dried under vacuum at 100°C overnight and then subjected to the subsequent runs. The recyclability test was carried out under aerobic condition without any special air



SCHEME 4 Plausible mechanism of alcohol oxidation by Cu(II)SeNSe@imine-nanoSiO₂ (**Complex I**)

TABLE 6Comparative study of oxidation of alcohols with supported Cu catalysts

Entry	Catalyst	Catalyst recycle number	Reaction conditions	Yield/ conversion (%)	Reference
1	$[CuL_2-SiO_2]$ and $[CuL'2-SiO_2]$, 5 mg	5	H_2O_2 , CH_3CN , rt	30-98	[43]
2	Cu(II)-5CML Schiff base/ Fe ₃ O ₄ @SiO ₂ , 17 mg, (2 mol%)	6	TEMPO, H_2O/CH_2Cl_{2} , $45^{\circ}C$	77–92	[22]
3	CuNPs/NC, 20 mg (0.756 mol%)	5	TEMPO, H ₂ O, EG, rt	45-99	[32]
4	CuO-REC, 31 mg, 37.6 µmol	5	K ₂ CO ₃ , TEMPO H ₂ O, O ₂ as the oxidant at 50°C	60–99	[23]
5	Cu@imine-nanoSiO ₂ , 15 mg, 0.26 mol% Cu	5	TBHP, CH ₃ CN, 50 °C	67–98	[44]
6	Cu(II)/AK,5 mg	5	H ₂ O ₂ , H ₂ O, rt	56–98	[45]
7	Cu(II)SeNSe@-imine-nanoSiO _{2,} 10 mg (0.18 mol% of Cu)	5	H ₂ O ₂ , CH ₃ CN, 80°C	75–98	Our work

manipulation. A slight gradual decrease in product yield during the course of reactions might be either physical change or catalyst leaching due to subsequent recycling (Figure S12). ICP-AES analysis carried out with the filtrate obtained after fifth cycle showed no significant Cu leaching, substantiating that Cu was strongly embedded on the solid support.

To check the physical change of the catalyst during subsequent runs, we have performed SEM-EDX and PXRD analyses of the catalyst recovered after the fifth catalytic cycle, which revealed its initial morphology with same chemical composition even after fifth catalytic cycle (Figures S13–S15).

3.5 | Catalytic activity of Cu(II)Se-N-Seimine (Complex II) for oxidation alcohols to corresponding carbonyl compounds

A typical reaction (Table 5) was carried out with 6 mg (5 mol % of Cu) of the catalyst, 2 mmol of substrate (1-phenylethanol), 4 mmol oxidant and 4-ml solvent and found the best optimized condition such as acetonitrile as solvent and H_2O_2 as oxidant with 80°C temperature for 3 h (Table S1, SI).

Finally, a probable mechanism of alcohol oxidation reaction by **Complex I** has been proposed, which is as given below in Scheme 4.^[50-53]

The decrease of ESR signal intensity of the catalyst recorded after completion of a catalytic cycle affirmed conversion of Cu(II) to Cu(I) during reaction (Figure S16).

The catalytic performance of Cu(II)SeNSe@imine $nanoSiO_2$ was compared with some other reported Cubased catalysts (Table 6), and it was observed that in most cases, hazardous reagents such as TEMPO/TBHP/ CH_2Cl_2 were used to carry out the reactions.

4 | CONCLUSIONS

The present research work reports a novel nanosilicasupported six-coordinated Cu(II) complex with Se-N-Se pincer ligand. The identity of the complex has been ascertained with different spectroscopic techniques. The parallel and perpendicular g-components observed in the ESR spectrum of the Complex I is indicative of tetragonal distortion. In addition to this, few narrow superhyperfine lines have been detected with the g_{\perp} peak. This significant nature of EPR spectrum clearly supports nitrogen coordination with the Cu(II). The catalytic activity of as-prepared catalyst has been explored for oxidation of primary and secondary alcohols to their corresponding aldehydes or ketones in the presence of H₂O₂ as oxidant at 80°C in acetonitrile solution. The benzylic alcohols produced excellent yields, whereas aliphatic alcohols are less reactive and required long reaction time. This protocol offers several advantages such as short reaction time, environmentally benign mild reaction conditions, good to excellent yields and good stability of the catalyst. The catalyst could be easily separated from the reaction products and reused for at least five successive runs effectively. The potentiality of an analogous unsupported Cu(II) complex as catalyst for the same reaction was observed unsatisfactory.

ACKNOWLEDGMENTS

The authors gratefully acknowledge SAIF, STIC, Kochi University, Kochi, for ICP-AES analysis; SAIF IIT Bombay for ESR analysis; IIT Kanpur for x-ray photoelectron



16 of 17 WILEY _______ Chemistry

spectroscopic analytical facility; and DST-SAIF Cochin for TGA analysis. The authors thank UGC, New Delhi, for the SAP-DRS-I grant (2016–2021) awarded to the Department of Chemistry, Dibrugarh University.

AUTHOR CONTRIBUTIONS

Rajjyoti Gogoi: Conceptualization; data curation; formal analysis; investigation; methodology; resources; software; visualization. **Geetika Borah:** Conceptualization; data curation; formal analysis; investigation; resources; supervision.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Rajjyoti Gogoi D https://orcid.org/0000-0002-5555-6693 Geetika Borah D https://orcid.org/0000-0002-5781-1694

REFERENCES

- N. Gogoi, P. Bordoloi, G. Borah, P. K. Gogoi, *Catal. Lett.* 2017, 147, 539.
- [2] P. J. Figiel, A. M. Kirillov, M. F. C. Guedes Da Silva, J. Lasria, A. J. L. Pombeiro, *Dalt. Trans.* 2010, *39*, 9879.
- [3] B. R. Kim, J. S. Oh, J. Kim, C. Y. Lee, Catal. Lett. 2016, 146, 734.
- [4] D. Datta, G. Halder, J. Polym. Environ. 2019, 27, 710.
- [5] H. Unver, I. Kani, J. Chem. Sci. 2018, 130, 33.
- [6] F. Cardona, C. Parmeggiani, C. Matassini, *Green Chem.* 2017, 19, 2030.
- [7] S. Hazra, E. Malik, A. Nair, V. Tiwari, P. Dolui, A. J. Elias, *Chem. - Asian J.* 2020, 15, 1916.
- [8] R. Gogoi, R. Saikia, G. Borah, J. Organomet. Chem. 2019, 897, 80.
- [9] C. Wu, B. Liu, X. Geng, Z. Zhang, S. Liu, Q. Hu, Polyhedron 2019, 158, 334.
- [10] J. Kim, S. S. Stahl, ACS Catal. 2013, 3, 1652.
- [11] M. B. Gawande, A. Goswami, F. X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R. S. Varma, *Chem. Rev.* **2016**, *116*, 3722.
- [12] Y. W. Jiang, K. Chai, Y. Q. Wang, H. D. Zhang, W. Xu, W. Li, Y. Shi, ACS Appl. Nano. Mater 2019, 2, 4435.
- [13] A. Kumar, G. Kumar Rao, A. K. Singh, RSC Adv. 2012, 2, 12552.
- [14] D. Das, P. Singh, M. Singh, A. K. Singh, Dalt. Trans. 2010, 39, 10876.
- [15] F. J. Morales-Leal, J. Rivera De la Rosa, C. J. Lucio-Ortiz, D. B. Martínez, D. de Haro Del Rio, M. A. Garza-Navarro, D. X. Martínez-Vargas, *Appl. Catal. A Gen.* 2018, 562, 184.

- [16] T. Rahman, G. Borah, P. K. Gogoi, J. Chem. Sci. 2019, 131, 4.
- [17] H. Zhao, B. Huang, Y. Wu, M. Cai, J. Organomet. Chem. 2015, 797, 21.
- [18] S. Pramanik, M. R. Das, D. Das, P. Das, *ChemistrySelect* 2017, 2, 4577.
- [19] A. Bhaumik, R. Kumar, J. Chem. Soc., Chem. 1995, 349.
- [20] Q. Cao, L. M. Dornan, L. Rogan, N. L. Hughes, M. J. Muldoon, *Chem. Commun.* 2014, 50, 4524.
- [21] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, Chem. Soc. Rev. 2014, 43, 3480.
- [22] N. Pérez-Almeida, M. González-Dávila, J. M. Santana-Casiano, A. G. González, M. S. Tangil, *Environ. Sci. Technol.* 2013, 47, 1239.
- [23] O. Das, T. K. Paine, Dalt. Trans. 2012, 41, 11476.
- [24] X. Liu, Q. Xia, Y. Zhang, C. Chen, W. Chen, J. Org. Chem. 2013, 78, 8531.
- [25] M. Aghajani, N. Monadi, Appl. Organomet. Chem. 2018, 32, 1.
- [26] W. Liu, J. Yang, J. Cai, Res. Chem. Intermed. 2019, 45, 549.
- [27] M. Nandi, P. Roy, H. Uyamac, A. Bhaumik, *Dalt. Trans.* 2011, 40, 12510.
- [28] S. M. Islam, P. Mondal, S. Mukherjee, A. S. Roy, A. Bhaumik, *Polym. Adv. Technol.* 2011, 22, 933.
- [29] P. Neves, A. A. Valente, Z. Lin, Eur. J. Inorg. Chem. 2020, 2020, 1172.
- [30] M. Cheng, M. Qin, L. Sun, L. Liu, Q. Liu, X. Tang, *Dalt. Trans.* 2020, 49, 7758.
- [31] A. J. Lemessa, Int. J. Mater. Sci. Appl. 2017, 6, 37.
- [32] E. Rafiee, S. Shahebrahimi, M. Feyzi, M. Shaterzadeh, Int. Nano Lett. 2012, 29, 1.
- [33] I. M. Joni, L. Nulhakim, M. Vanitha, C. Panatarani, J. Phys. Conf. Ser. 2018, 1080, 012006.
- [34] S. Sultana, G. Borah, P. K. Gogoi, Appl. Organomet. Chem. 2019, 33, 1.
- [35] S. Sultana, G. Borah, P. K. Gogoi, Catal. Lett. 2019, 149, 2142.
- [36] K. Kostiantyn Kulyk, L. Liana Azizova, J. M. Cunningham, L. Mikhalovska, M. Borysenkoa, S. Mikhalovsky, J. Mater. Chem. B 2020, 8, 4267.
- [37] P. Nyamukamba, L. Tichagwa, J. C. Ngila, L. Petrik, J. of Photochem and Photobiol a: Chemistry 2017, 343, 85.
- [38] G. Yang, J. Ma, W. Wang, J. Zhao, X. Lin, L. Zhou, X. Gao, *Catal. Lett.* **2006**, *112*, 83.
- [39] A. Dutta, M. Chetia, A. A. Ali, A. Bordoloi, P. S. Gehlot, A. Kumar, D. Sarma, *Catal. Lett.* **2019**, *149*, 141.
- [40] F. R. Díaz, C. O. Sánchez, M. A. del Valle, L. Ugalde, L. Gargallo, Synth. Met. 1999, 105, 161.
- [41] K. Helios, A. Pietraszko, W. Zierkiewicz, H. Wójtowicz, D. Michalska, *Polyhedron* 2011, 30, 2466.
- [42] Y. Gong, M. Zhou, Chem. Rev. 2009, 109, 6765.
- [43] S. P. Sovilj, G. Vuèkovic, V. M. Leovac, D. M. Minic, Polish J. Chem. 2000, 74, 945.
- [44] K. Malek, M. Vala, J. S. Kozlowskac, L. M. Proniewiczad, New J. Chem. 2004, 28, 477.
- [45] M. Lavanya, M. Jagadeesh, J. Haribabu, R. Karvembu, H. R. Rashmi, U. P. Maheswari Devi, A. V. Reddy, *Inorganica Chim. Acta.* 2018, 469, 76.
- [46] E. Garribba, G. Micera, J. Chem. Educ. 2006, 83, 1229.
- [47] S. M. Lomnicki, H. Wu, S. N. Osborne, J. M. Pruett, R. L. McCarley, E. Poliakoff, B. Dellinger, *Mater. Sci. Eng.*, B 2010, 175, 136.

- [48] T. Tsoncheva, G. Issa, T. Blasco, M. Dimitrov, M. Popova, S. Hernández, D. Kovacheva, G. Atanasova, J. M. López Nieto, *Appl. Catal. A Gen.* 2013, 453, 1.
- [49] J. Zhang, L. Fan, Y. Zhu, Y. Xu, J. Liang, D. Wei, Y. Qian, *Nanoscale* 2014, 6, 12952.
- [50] N. Gogoi, T. Begum, S. Dutta, U. Bora, P. K. Gogoi, *RSC Adv.* 2015, 5, 95344.
- [51] T. F. S. Silva, L. M. D. R. S. Martins, Molecules 2020, 25, 748.
- [52] M. Hakimi, H. Vahedi, R. Takjoo, A. Rezaeifard, Int. J. ChemTech Res. 2012, 4, 1658.
- [53] R. Mirsafaei, M. M. Heravi, T. Hosseinnejad, S. Ahmadi, *Appl. Organomet. Chem.* **2016**, *30*, 823.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

How to cite this article: R. Gogoi, G. Borah, *Appl* Organomet Chem **2021**, e6416. <u>https://doi.org/10.</u> 1002/aoc.6416