

Nanoporous Silica Supported Novel Copper (II) Thiosemicarbazone Complexes as Selective and Reusable Catalysts for Oxidation of Alcohols Using H₂O₂

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Abstract: Two novel copper (II) complexes containing thiosemicarbazones supported on nanoporous silica gel, [CuL₂-SiO₂] and [CuL'₂-SiO₂] were prepared by direct sol-gel method. The material was characterized by physico-chemical characterization, SEM and TEM methods. These complexes were found to be competent catalysts for selective oxidation of primary and secondary alcohols using hydrogen peroxide as an environmentally friendly oxidant. The catalysts could easily be recycled and reused without noticeable loss of activity.

Keywords: Nanoporous silica, thiosemicarbazone, copper complexes, oxidation, alcohol, hydrogen peroxide.

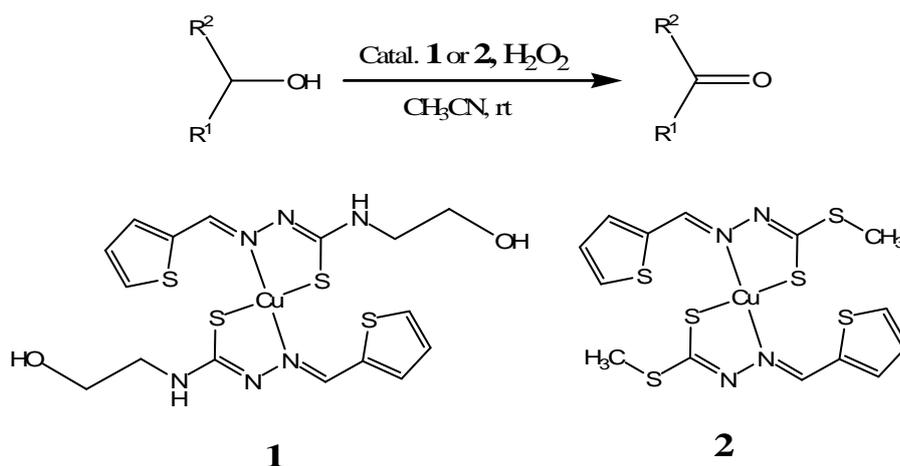
Introduction and Experimental

Nanosized materials have played an important role in heterogeneous catalysis for many years long before their application in nanotechnology. An important goal in catalyst research is to generate understanding of catalytic phenomena and to develop techniques that enable achieving perfect (100%) selectivity and desirable activity in a chemical reaction.¹⁻²

Introduction of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors (like PhIO, O₂, H₂O₂, t-BuOOH, or NaOCl) into various organic molecules, under mild conditions,

has been an intricate challenge in chemical and biological catalysis.³ As possible alternative catalysts in many oxidation and hydroxylation reactions,⁴⁻¹⁰ attentions have been paid to the inorganic mimics of enzymes which are metal complexes containing porphyrin, macrocycle salen, and phthalocyanine ligands.¹¹⁻¹⁵ Chiral Schiff base complexes are more selective in various reactions such as oxidation, hydroxylation, aldol condensation and epoxidation¹⁶.

The heterogeneous catalysts have some inherent advantages over their homogeneous counterpart in that their separation from reaction mixture and purifying of the products are more convenient.



Scheme . Oxidation of alcohol with hydrogen peroxide catalyzed by 1 and 2.

Therefore, in recent years many scientific groups are motivated to apply solid support in the heterogenization of some transition metal catalysts. In their method, the homogeneous catalysts were immobilized onto inorganic solids¹⁷⁻²³ and organic polymers.²⁴⁻²⁷

In the present research work, two thiosemicarbazone copper (II) complexes have been synthesized and characterized (Scheme). They were supported on nanoporous silica and used as reusable heterogeneous catalysts in the selective oxidation of alcohols to carbonyl compounds using hydrogen peroxide as an environmentally friendly oxidant (Scheme)²⁸.

Instrumentation

¹H NMR spectra were recorded on an instrument operating at 250 MHz using DMSO-*d*₆ as the solvent with TMS as the internal standard. C, H, N and S analyses were obtained with a Thermo Finnigan Flash Elemental Analyzer; model 1112EA. FT-IR spectra were recorded on 8400 Model SHIMADZU FT-IR spectrometer (4000-400 cm⁻¹). UV-Vis absorption spectrum was measured on a SHIMADZU model 2550 spectrophotometer in dimethylformamide solutions. Purity determinations of the products were accomplished by GC on a Shimadzu GC-16A instrument using a 25 m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column.

Preparation of ligands

N-(2-hydroxyethyl)-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide, HL, and Methyl-2-(thiophen-2-ylmethylene)hydrazine carbodithioate, HL' were prepared using a reported procedure [29, 30]. For preparation of *N*-(2-hydroxyethyl)-2-

(thiophen-2-ylmethylene) hydrazinecarbothioamide a solution of methyl 2-(thiophen-2-ylmethylene)hydrazinecarbo-dithioate (1.7 g, 7.86 mmol) in ethanol (10 ml) was treated with 2-aminoethanol (0.5 ml, 7.86 mmol) and refluxed for 72 h. The solution was chilled (overnight) and a pale yellow precipitate was separated, collected and washed well with cold ethanol. The compound was recrystallized from ethanol and dried in vacuo over silica gel.

HL: pale yellow, Yield: 0.93 g (52%). m.p.: 147.5 °C. Anal.Calc. for C₈H₁₁N₃OS₂ (229.3 g mol⁻¹): C, 41.90; H, 4.83; N, 18.32; S, 27.96%. Found: C, 41.65; H, 4.84; N, 19.09; S, 27.15%. IR spectrum in KBr, cm⁻¹: (OH) 3358w, (NH) 3165, 3053m, (C=N)+ (C=C)+ (NH₂) 1547s, (C=S) 1277m, (C-O) 1225m, (C-N) 1128m, (N-N) 1051s, (C=S) 869w, (ring) 623s. UV/Vis (DMF), *max*, nm (log ε, L mol⁻¹ cm⁻¹): 269 (4.70), 334 (4.71), 350 (4.59). ¹H NMR (250 MHz, DMSO-*d*₆): =11.54 (s, 1H, N²H; exchangeable with D₂O), 8.25 (s, 1H, C⁵H(, 7.65) d, 1H, C¹H(, 7.43) d, 1H, C³H(, 7.11) t, 1H, C²H(, 4.85 (s, 1H, N³H; exchangeable with D₂O), 3.58 (s, 5H, C⁷H₂C⁸H₂O¹H; OH exchangeable with D₂O). ¹³C NMR (250 MHz, DMSO-*d*₆): =177.16 (C⁶), 139.01 (C⁴ (, 137.89 (C³ (, 131.18) C¹ (, 129.23) C² (, 128.44) C⁵ (, 59.69 (C⁸), 46.41 (C⁷). UV-Vis (DMF), *max*, nm (log ε, L.mol⁻¹.cm⁻¹): 269 (4.70), 334 (4.71), 350 (4.59).

Preparation of CuL₂ complex, bis(*N*-(2-hydroxyethyl)-2-(thiophen-2-ylmethylene)hydrazine carbothio-amido)copper(II), (1)

To a warm ethanol solution (5 ml) of ligand (0.1 g, 0.43 mmol) was added the Cu(OAc)₂.2H₂O (0.054 g, 0.27mmol) in methanol (5 ml). The mixture was

refluxed for 2 h and the product was separated by filtration, washed with cold ethanol and dried. The structure of the complex is given in Scheme .

CuL₂: Dark brown, Yield: 0.089 g (73% based on HL). m.p.: 181 °C. Molar conductance ($1 \times 10^3 \text{ mol L}^{-1}$; DMF): $2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Anal. Calc. for $\text{C}_{16}\text{H}_{20}\text{N}_6\text{CuO}_2\text{S}_4$ ($520.17 \text{ g mol}^{-1}$): C, 36.94; H, 3.88; N, 16.16% Found: C, 36.27; H, 3.84; N, 16.66%. IR spectrum in KBr, cm^{-1} : (O-H) 3414m; (N-H) 3103w; $\nu(\text{C-H})$ 2931m; (C=N) 1571m; (C=N)+ (C=C)+ (NH₂) 1529s; (C=S) 1247m; (C-O) 1244s; (N-N) 1066m; (C=S) 827m; (ring) 623w. UV/vis (DMF), λ_{max} , nm (log ϵ , $\text{L mol}^{-1} \text{ cm}^{-1}$): 272 * (4.18), 367 n * (4.45), 792 d d (2.23). UV-Vis (DMF, λ_{max} (nm)/): 564/241 (d d).

Preparation of, CuL₂ complex, bis(methyl 2-(thiophen-2-ylmethylene)hydrazinecarbodithioate)copper(II), (2)

Methyl 2-(thiophen-2-ylmethylene)hydrazine carbodithioate (0.1 g, 0.5 mmol) was added to $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.05 g, 0.25 mmol) in methanol (4 ml). The mixture was refluxed for 1 h and the product was separated by filtration, washed with cold methanol and dried. A light brownish compound was obtained. The structure of the complex is given in Scheme .

CuL₂: Light brown, $\text{C}_{14}\text{H}_{14}\text{CuN}_2\text{S}_6$ ($492.88 \text{ g mol}^{-1}$), Yield: 0.14 g (61.7% based on ethanalamine) m.p.: 233 °C dec. IR (KBr), cm^{-1} : (C-H) 3093m; $\nu(\text{CH}_3)$ 2916m; (C=N) 1589m; (CSS) 1041; (C=S) 771w. UV/Vis (DMF), λ_{max} , nm (log ϵ , $\text{L mol}^{-1} \cdot \text{cm}^{-1}$): 303 (3.67), 358 (4.02), 467 (2.83).

Preparation of GN/Silica composite

The GN/Silica was prepared using tetraethyl orthosilicate (TEOS, 99%, Aldrich), as the silica source, Gelatin (GN) as organic source as follows: one mole TEOS was mixed with 4 mole of ethanol and 4 mol of distilled water and, after being stirred for about 30 min, 0.01 mol hydrochloric acid (HCl, 37 w% in water) was added into the solution and then the solution was stirred at room temperature for 1 h. The organic component, Gelatin solution 12 w%, that previously prepared at 45 °C with magnetic stirring for about 2h, is added to the previous solution and the mixture was stirred for 24 h. The gel either was dried at 70 °C for 20 h and then calcinated at 650 °C for 7h, or at the temperature and time predetermined for a specific experiment, with a temperature gradient 30/min.

Preparation of nanoporous silica gel supported Cu (II) thiosemicarbazone complexes, catalysts 1 and 2

Silica composite was activated by refluxing in concentrated hydrochloric acid, and then washed thoroughly with deionized water, and dried before undergoing chemical surface modification. Hydrated silica was then added to Schiff base complex solutions, and the mixture was stirred over night. The solvent was removed using a rotary evaporator, and the resulting olive green solid dried at 90 °C over night. The final product was washed with MeOH and water until the washings were colorless. Further drying of solid products was carried out in an oven at 90 °C for 7h.

Typical procedure for oxidation of benzyl alcohol with H₂O₂ catalyzed by supported Cu(II) complexes, (1and 2)

To a solution of 1 mmol of benzyl alcohol (0.11 g) in 5 ml of acetonitrile containing 0.05 g of heterogeneous catalysts **1** or **2** was added 3 mmol of H₂O₂ (30%) and the reaction mixture was stirred at room temperature for a specified time. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the suspension was filtered; the solvent was evaporated and washed with brine. The product, benzaldehyde, was obtained in 93% yield (0.1 g). IR, $\nu_{\text{C=O}} = 1703 \text{ cm}^{-1}$; ¹H NMR, (CDCl_3) 10 (1H, s, CHO), 7.5-7.7 (5H, m, Ar) ppm.

Catalysts reuse and stability

The heterogeneous catalysts could be reused consecutively at least for five times in the oxidation of benzyl alcohol without significant loss of its activity (average benzaldehyde yields was 92%). In all four repetitions and after end of each step the amount of copper leached into the filtrates was determined by atomic absorption spectrometry.

Results and discussion

According to spectral and elemental analysis, the bis(methyl 2-(thiophen-2-ylmethylene) hydrazine carbodithioate) copper(II) and bis (N-(2-hydroxy ethyl)-2-(thiophen-2-ylmethylene) hydrazinecarbo thioamido)copper(II) complexes are square planar geometry (Scheme). This Cu-complex was encapsulated to nano-silica matrix as a sol-gel process so that new heterogeneous catalysts were successfully formed. IR spectral assignments of the ligands and the complexes are listed in experimental section. The IR spectrum of the ligand exhibits a band at 3053 cm^{-1} assigned to (N-H) vibration, disappears in the spectra of

complex, providing strong evidence for ligand coordination to the metal center in the deprotonated thiolate form [30]. The (C=S) vibration for free ligand assigned at 1277 cm^{-1} moved to 1247 cm^{-1} . This blue shift supports the coordination through the thione form. The (C-N) band for Cu(II)-complexes indicates blue shift with respect to ligand, supporting presence of thiol form. The N-N stretching vibration of the thiosemicarbazone at 1066 cm^{-1} does not shift after coordination. The band in the range of 1244 cm^{-1} corresponds to (C-O) in the complex [32].

The electronic spectral assignments of the ligand and Cu(II)-complexes in DMF are given in experimental section. In the spectrum of the ligand two bands at 350 and 334 nm are attributed to

$n \rightarrow \pi^*$ transition of thiophene and thioamide moiety, respectively. A band for $\pi \rightarrow \pi^*$ transition is appeared at 270 nm in ligand spectrum, and show blue shift to 367 cm^{-1} after coordination. This confirms that sulfur atom is bound to central atom. The tailing of charge transfer bond into visible region obscures the weak d-d absorption bands so that only one d-d transition at 792 nm can be observed [31].

The SEM micrograph of catalyst **1** is shown in Fig. 1. The SEM results indicate that the complex has been successfully tethered onto the surface of nanosilica. The TEM image of catalyst **1** (Fig. 2) clearly indicates mesoporous morphology of the material. In addition, it reveals that the matrix have an average diameter of about 10 nm.

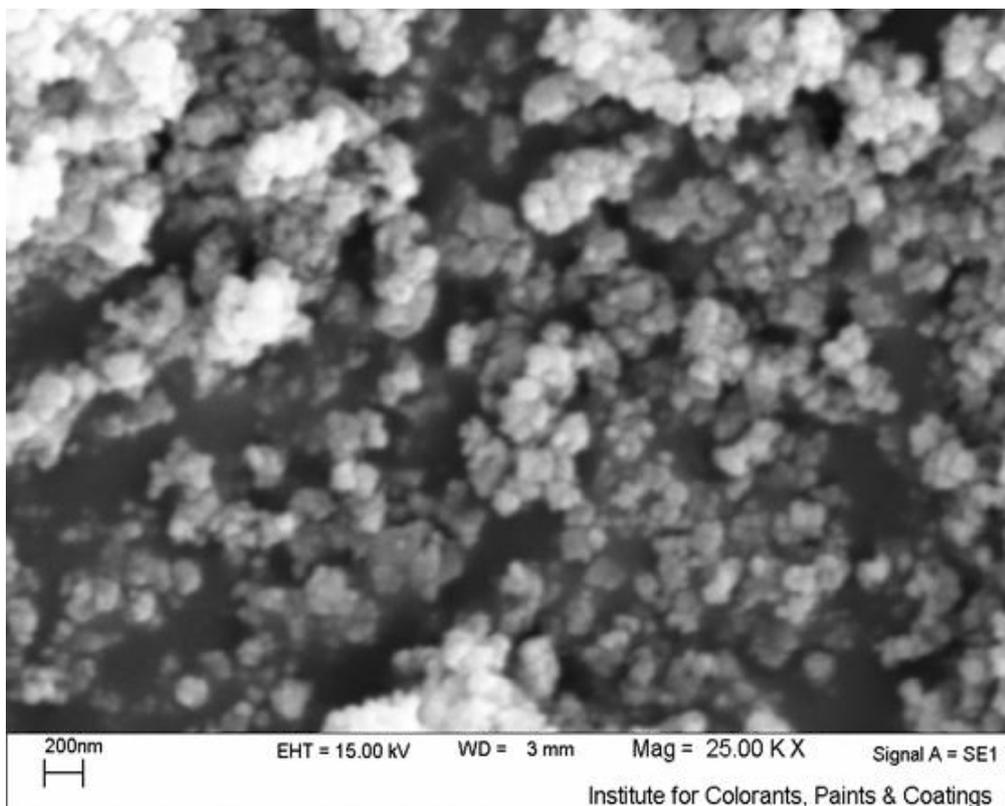


Fig. 1 The SEM micrograph of nanoporous supported CuL₂ (**1**).

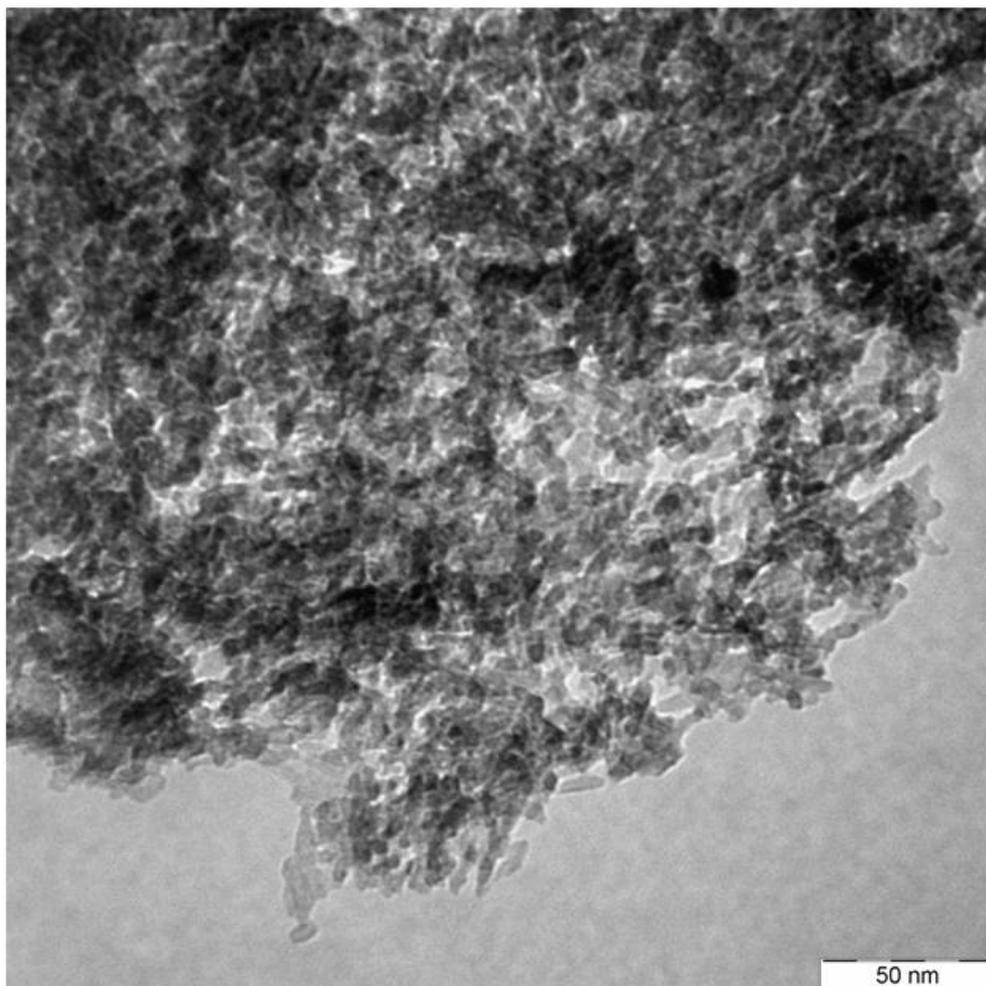


Fig. 2 The TEM image of nanoporous supported CuL_2 (**1**).

Hence, catalyst **1** could be attached to the surface of the nano-silica particle, and dark points on TEM confirm the attachment. These dark points were Cu(II) complex distributed on the surface of nano-silica support. It is deduced that more sites are available for substrates therefore enhance the catalytic activity of the nano catalyst **1**.

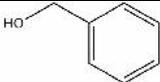
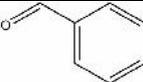
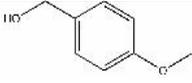
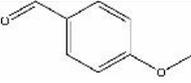
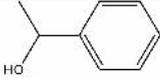
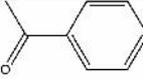
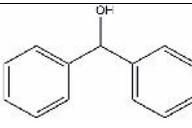
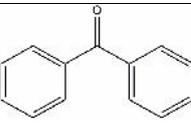
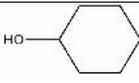
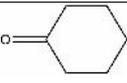
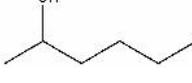
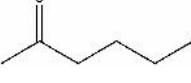
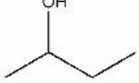
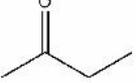
Catalytic activity of Cu-complexes

The oxidation of alcohols to the corresponding carbonyl compounds is one of the most frequently used and important transformation in organic chemistry as demonstrated by a plethora of methods and procedures that have been developed for this purpose. Unfortunately, the traditional methods for oxidation of alcohols suffer from the drawbacks such as the use of at least a stoichiometric amount of oxidants and bring about a large quantity of harmful by-products. Thus, from the standpoint of the so-called green and sustainable chemistry, another approach to construct cleaner catalytic systems for oxidation of alcohols using molecular oxygen and hydrogen

peroxide has been becoming increasingly attractive in recent years [32].

Our preliminary experiments were addressed to the oxidation of benzyl alcohol as a model reaction, to determine the best conditions with respect to yield, reaction time and temperature. The use of 1 mmol of benzyl alcohol and 3 mmol of H_2O_2 in the presence of a catalytic amount of the complexes (0.05 g) gave benzaldehyde in 98% yield (GC) within 30 min at room temperature. Based on the optimized reaction conditions, the present protocol was applied to a variety of primary and secondary aliphatic and benzylic alcohols (Table). All alcohols oxidized smoothly to the corresponding aldehydes and ketones in good/excellent yields (entries 1-4). However, the catalysts were more effective for the oxidation of benzylic alcohols than those of aliphatic ones. Selectivity of oxidation system was notable and no over oxidation of aldehydes (to carboxylic acids) and ketones (Baeyer-Villiger oxidation) was observed under the catalytic influence of both catalysts.

Table: Oxidation of alcohols with H₂O₂ catalyzed by 1 and 2.^a

Entry	Alcohol	Product	Yield (%) ^{b,c}	
			Catal. 1	Catal. 2
1			98 (93) ^d	85 (76) ^d
2			99	90
3			95 (87) ^d	95 (90) ^d
4			90	88
5			85	58
6			40	43
7			35	40
8			30	35
9			25	33
10			47	50
11			30	40
12			38	40

^aThe reactions were run at rt using 0.05 g of heterogeneous catalysts and 3 eq. of H₂O₂.

^bThe yields were determined by GC after 30 min for entries 1-4 and 60 min for others.

^c100% selectivity were obtained for products according to GC and ¹H NMR.

^dIsolated yields.

The moderate/high yields of carbonyl compounds obtained by this catalytic oxidation system at room temperature in desired times (<60 min) indicates the high efficiency and also relative stability of title Cu (II) complexes in combination with hydrogen peroxide. The catalyst proved to be

reusable for at least four times in the oxidation of benzyl alcohol without noticeable loss of activity. The average GC yields of benzaldehydes for four runs were 95% and no Cu (II) ions were detected in the reaction solutions according to atomic absorption analysis.

Conclusions

In conclusion, the catalytic performance of two novel copper (II) thiosemicarbazone complexes supported on nanoporous silica by direct sol-gel method in the oxidation of alcohols using hydrogen peroxide was established. The good/high yields and excellent selectivity were achieved in the oxidation of a wide variety of alcohols at room temperature. The heterogeneous copper catalysts could be easily recycled and reused without noticeable loss of activity. The employment of

hydrogen peroxide as an environmentally benign oxygen source as well as easy reusability of catalysts in this mild and selective oxidation method makes it an attractive methodology for practical goal.

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