Application of Nickel(II) Thiosemicarbazone Supported on Nano Porous Silica as a Catalyst for Selective Oxidation of Alcohols

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Abstract: A new encapsulated material [NiL2-SiO2] was prepared by direct sol-gel method. The material was characterized by fourier-transform (FTIR), proton nuclear magnetic resonance (1H NMR), ultraviolet-visible (UV-Vis), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. The characterization results reveal that Ni-complex was highly dispersed into silica matrix and its structure remained intact after formation of the material. The material was found to be highly active and reusable for selective oxidation of primary and secondary alcohols. Under the optimal reaction conditions, primary and secondary alcohols were prevalingly oxidized to their corresponding acids or ketones. Moderate and efficient oxidation of primary and secondary alcohols with hydrogen peroxide catalyzed by NiL2, [bis(N-(2-hydroxyethyl)-2-(thiophene-2-ylmethylene)hydrazinecarbothioamido) nickel(II)], supported on mesoporous [NiL2-SiO2], at room temperature were reported.

Key words: Selective oxidation, encapsulated, nickel thiosemicarbazone complex, hydrogen peroxide, alcohols.

1. Introduction

Nanotechnology refers to techniques that offer the ability to design, synthesize, and control materials at scales ranging from 1 to 100 nm. Researches on the subject date back several decades, since then material synthesis at nanometer scale has become a routine practice for scientists. Recently, the development of cutting-edge technologies and techniques in synthesis and characterization of materials and devices at the nanoscale has resulted in enormous popularity of nanotechnology. Moreover, nanotechnology is a breakthrough of recent century which would hopefully push back the frontiers in a variety of fields such as medicine, electronic, chemistry, and engineering. Hence, there are many reports of new researches about it and its applications in scientific databases. Nanosize metal particles have played an important role in heterogeneous catalysis for many years long before their application in nanotechnology. These items justify such a huge investigation on heterogeneous catalysis [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]. Using

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transition metal Schiff base for oxidation reaction is interesting and in practice because of easy synthesis, various structural fashion and potency to coordinated to transition metal [16].

Although few heterogeneous catalysts have higher catalytic activity than their corresponding homogeneous counterpart, as a disadvantage, most of them generally cause partial loss of activity [17, 18]. However 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. 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 solids [19-23] and organic polymers [24-27].

In this work, a new thiosemicarbazone nickel complexes have been synthesized and characterized. This complex immobilized on silica nanoporous as a catalyst. This supported nickel(II) catalyst was used successfully in the oxidation of alcohols with hydrogen peroxide at room temperature. Hydrogen peroxide is the desired green oxidant with a high potential for production of active oxygen, with no interference, and it is economical, recyclable, mild and efficient. Therefore, it is used here in oxidant of primary and secondary alcohols (Fig. 1) [28].

2. Experiment

2.1 Materials and Instrumentation

All chemicals were Aldrich analytical grade and were used as received. 1H NMR spectra were recorded on an instrument operating at 100 MHz using DMSO-<i>d</i><sub>6</sub> 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. FTIR spectra were recorded on 8400 Model SHIMADZU FTIR spectrometer (400-4,000 cm<sup>-1</sup>). UV-Vis absorption spectrum was measured on a SHIMADZU model 2550 spectrophotometer in dimethylformamide solutions.

2.2 Preparation of Ligand

<math>\text{N-(2-hydroxyethyl)-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide was prepared as following: methyl 2-(thiophen-2-ylmethylene)hydrazinecarbodithioate was prepared using a reported procedure [29]. 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 silicagel.}</math>

<math>\text{HL: pale yellow, Yield: 0.93 g (52%). m.p.: 147.5 °C. Anal. Calc. for C}_{8}H_{11}N_{3}OS_{2} (229.3 g·mol<sup>-1</sup>): 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<sup>-1</sup>: ν(OH) 3,358 w, ν(NH) 3,165, 3,053 m, ν(C=N) + ν(C=C) + δ(N-H) 1,547 s, ν(C=S) 1,277 m, ν(C-O) 1,225 m, ν(C=N) 1,128 m, ν(N-N) 1,051 s, δ(C=S) 869 w, ρ(ring) 623 s. UV/Vis (DMF), λ<sub>max</sub>, nm (log ε, L·mol<sup>-1</sup>·cm<sup>-1</sup>): 269 (4.70), 334 (4.71), 350 (4.59). 1H NMR (250 MHz, DMSO-<i>d</i><sub>6</sub>): δ = 11.54 (s, 1H, N-H; exchangeable with D<sub>2</sub>O), 8.25 (s, 1H, C<sub>5</sub>H), 7.65 (d, 1H, C<sub>1</sub>H), 7.43 (d, 1H, C<sub>3</sub>H), 7.11 (t, 1H, C<sub>2</sub>H), 4.85 (s, 1H, N-H; exchangeable with D<sub>2</sub>O), 3.58 (s, 5H, C<sub>7</sub>H<sub>2</sub>C<sub>8</sub>H<sub>2</sub>O<sub>1</sub>H; OH exchangeable with D<sub>2</sub>O). 13C NMR (250 MHz, DMSO-<i>d</i><sub>6</sub>): δ =177.16 (C<sub>6</sub>), 139.01 (C<sub>4</sub>), 137.89 (C<sub>3</sub>), 131.18 (C<sub>1</sub>), 129.23 (C<sub>2</sub>), 128.44 (C<sub>5</sub>), 59.69 (C<sub>8</sub>), 46.41 (C<sub>7</sub>).}</math>
2.3 Preparation of Bis[N-(2-hydroxyethyl)-2-(thiophen-2-ylmethylene)hydrazinecarbothio-amido] nickel(II) NiL₂ Complex

To a warm ethanol solution (20 mL) of ligand (0.46 g, 2 mmol), the nickel(II) acetate (0.25 g, 1 mmol) was added in 1:2 molar ratios. The mixture was refluxed for 2 h and the product was separated by filtration, washed with cold ethanol and dried over silicagel. The structure of the complex is given in Fig. 2.

Dark brown, Yield: 0.08 g (66% based on HL). m.p.: 225 °C. Molar conductance (10⁻³ M, DMF) 9 ohm⁻¹ cm² mol⁻¹. Anal. Calc. for C₁₆H₂₀N₆NiO₂S₄ (515.32 g mol⁻¹): C, 37.18; H, 3.85; N, 16.31; S, 24.89%. Found: C, 37.29; H, 3.91; N, 14.93; S, 20.89. IR spectrum in KBr, cm⁻¹: ν(OH) 3,201 m, ν(NH) 3,030 m, ν(C=N) + ν(C=C) + δ(N-H) 1,510 s, ν(C=S) 1,288 m, ν(C-O) 1,244 m, ν(C-N) 1,205 w, ν(N-N) 1,066 m, δ(C=S) 840 w, ρ(ring) 623 w. UV/Vis (DMF), λ_max, nm (log ε, L mol⁻¹·cm⁻¹): 267 (4.59), 337 (4.52), 359 (4.50)sh, 382 (4.44)sh, 618 (2.30). ¹H NMR (100 MHz, DMSO-d₆): δ = 7.9 (d, 1H, C₁H), 7.72 (s, 1H, C²H), 7.6 (d, 1H, C³H), 7.15 (t, 1H, C⁴H), 4.7 (s, br, 1H, N⁵H; exchangeable with D₂O), 3.6-3.3 (s, 5H, C⁶H₂C⁷H₂O¹H; OH exchangeable with D₂O).

2.4 Preparation of Ge/Silica Composite

The Ge/Silica was prepared using tetraethyl orthosilicate (TEOS, 99%, Aldrich), as the silica source, Gelatin as organic source, Ethanol (EtOH), as solvent, distilled water and HCl were prepared as follows: one mole TEOS was mixed with 4 mol 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. For the organic component, Gelatin solution 12 w% that previously prepared at 45 °C with magnetic stirring for about 2 h is added to the previous solution and the mixture was stirred for 24 h. The xerogel was dried at 70 °C for 20 h and then calcinated at 750 °C for 7 h, or at the temperature and time predetermined for a specific experiment, with a temperature gradient 30/min.

2.5 Preparation of Heterogenized Ni(II) Thiosemicarbazone Complex, Catalyst 1

Silica composite was activated by refluxing in concentrated hydrochloric acid, then washed thoroughly with deionized water, and dried before undergoing chemical surface modification. Hydrated silica was then added to Schiff base complex solution, and the mixture was stirred over night. The solvent was removed using a rotary evaporator, and the resulting olive green solid dried at 80 °C over night. The final product was washed with MeOH and water until the washings were colorless. Further drying of solid product was carried out in an oven at 80 °C for 8 h.

2.6 Procedure for Oxidation of Alcohols with H₂O₂ Catalyzed by Supported Ni(II) Complex, Catalyst 1

In a round-bottom flask (25 mL) equipped with a magnetic stirrer, a solution of 1 mmol of alcohol in 5 mL of acetonitril was prepared. To this solution, 0.05 mmol of catalyst 1 and 20 mmol of H₂O₂ (30%) were added and the reaction mixture was stirred at room temperature for a specified time. The progress of the reaction was monitored by TLC.

After completion of the reaction, the suspension was filtered; the solvent was evaporated and washed with brine. IR and ¹H NMR spectral data were used to confirm the identities of the products.

2.7 Catalyst Reuse and Stability

This catalyst can be reused consecutively four times in the oxidation of benzyl alcohol as a model substrate.
in 97% yield without significant loss of its activity. In all four repetitions and after end of each step the amount of nickel leached into the filtrates was determined by atomic absorption spectrometry.

3. Results and Discussion

According to spectral and elemental analysis, the bis(N-(2-hydroxyethyl)-2-(thiophen-2-ylmethylene)hydrazinecarbothioamido)nickel(II) complex is square planar geometry (Fig. 2). This Ni-complex was encapsulated to nano silica matrix as a sol-gel process so that a new heterogeneous catalyst was successfully formed.

3.1 Catalyst Characterization

IR spectral assignments of the ligand and the complexes are listed in experimental section.

The IR spectrum of the ligand exhibits a band at 3,053 cm\(^{-1}\) assigned to \(\nu(N–H)\) vibration, disappears in the spectra of complex, providing strong evidence for ligand coordination to the metal center in the deprotonated thiolate form. The \(\nu(C=S)\) vibration for free ligand assigned at 1,276 cm\(^{-1}\) moved to 1,290 cm\(^{-1}\) that this red shift supports the coordination through the thione form. The \(\nu(C-N)\) band for Ni(II)-complex indicates blue shift with respect to ligand, supporting presence of thiol form. The N-N stretching vibration of the thiosemicarbazone at 1,051 cm\(^{-1}\) shift to 1,068 cm\(^{-1}\) after coordination. The band in the rage of 1,244 cm\(^{-1}\) corresponds to \(\nu(C-O)\) in the complex [30].

The electronic spectral assignments of the ligand and Ni(II)-complex in DMF are given in experimental section. In the spectrum of ligand two bonds at 350 and 334 nm are attributed to n→π* transition of thiophene and thioamide moiety, respectively. A band for π→π* transition is appeared at 270 nm in ligand spectrum, and show no considerable shift after coordination. After complexation, a new band at 382 nm corresponding to S→Ni(d) LMCT charge transfer was appeared. This confirms that sulfur atom is bound to central atom. The tailing of charge transfer bond into visible region obscures the very weak d-d absorption bands so that only one d-d transition at 618 nm is seen [31].

3.2 Scanning and Transmission Electron Microscopy (SEM and TEM)

The SEM micrograph of catalyst 1 is shown in Fig. 3a. The micrograph shows porous structure with a pore diameter of about 116 nm. SEM results indicate that complex has been successfully tethered onto the surface of nanosilica.

The TEM micrograph of catalyst 1 (Fig. 3b) clearly indicates mesoporous morphology of the material. In addition, it reveals that the matrix have an average diameter of about 20 nm.

Hence, catalyst 1 could be attached to the surface of the nano-Silica particle, and dark points on TEM

Fig. 3 The SEM micrograph (a) and TEM image (b) of heterogenized Ni(II)-complex.
Table 1  Oxidation of alcohols with H₂O₂ catalyzed by catalyst 1 at room temperature.

<table>
<thead>
<tr>
<th>No.</th>
<th>Alcohol</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Time (min)</th>
<th>Selectivity</th>
</tr>
</thead>
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<td><img src="image2" alt="Molecule" /></td>
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<td>95</td>
<td>90</td>
<td>100</td>
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<tr>
<td>3</td>
<td><img src="image5" alt="Molecule" /></td>
<td><img src="image6" alt="Molecule" /></td>
<td>98</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
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<td>98</td>
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<td>100</td>
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<td>480</td>
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</tr>
</tbody>
</table>
confirm the attachment. These dark points were Ni(II) complex distributed on the surface of nano-silica support. It is deduced that more sites are available for substrates which increase the catalytic activity of the nano catalyst 1.

3.3 Catalytic Reaction

Alcohols oxidation was used to investigate the catalytic ability of catalyst 1. This heterogeneous catalyst is applied for a wide variety of primary and secondary alcohols as shown in Table 1. In all reactions, the catalyst is showed to have a very good catalytic activity. The Ni(II) determination by atomic absorption confirmed that the complex was firmly entrapped in the matrix. Furthermore, in the reaction solutions no Ni(II) atoms were detected.

The catalyst had appropriate selectivity so that for primary alcohols from two probable acids and aldehydes products, only acids were generated. Usually, conversion of primary alcohols to carboxylic acids needs to a powerful oxidant such as KMnO₄, K₂Cr₂O₇, in harsh reaction condition.

So, mild reaction condition and green oxidant are advantages of this catalytic oxidant reaction. In addition, for secondary alcohols only ketones were made. In the absence of catalyst 1, the conversion reaction of alcohols to acids or ketones was much less efficient. Secondary benzoic alcohols oxidize faster than cycloalkanes. Aromatic alcohols with electron donating group reach faster than those ring with electron-withdrawing substitution. Selectivity of all reactions is very high and we do not observed any overoxidation (Baeyer-Villiger oxidation) on ketones.

4. Conclusions

In this study, we have demonstrated the effectiveness of a heterogenized new nickel(II) complex based on sol-gel catalyst for oxidation of different types of alcohols to carbonyl compounds with hydrogen peroxide. The catalyst has converted primary and secondary alcohols to acids and ketones, respectively. This catalyst has some advantages such as: High yields, mild reaction condition, short reaction times, operational simplicity, excellent selectivity, low cost and reusability.

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