



Catalytic activities of novel silica-supported multifunctional Schiff base ligand & metal complexes under microwave irradiation



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ABSTRACT

In this paper, a novel solid phase supported Schiff base ligand (L^1 : MDPMP) was prepared from 2-hydroxy-5-((2-methoxyphenyl)diazenyl) benzaldehyde (L : HMDB) and silica-gel, activated with 3-aminopropyltriethoxysilane (APTES). Cu (II), Co (II), Ni (II) and Mn (II) complexes of silica-supported ligand (L^1 : MDPMP) were obtained. The ligand and its four metal complexes were characterized by using NMR (^1H and ^{13}C), FT-MIR/FIR, elemental analysis, ICP-OES, TGA and Scanning Electron Microscope (SEM). Their catalytic performances in catalytic oxidation of cyclohexane were investigated for the selective oxidation of cyclohexane under microwave power. Silica-supported L^1 -Cu (II) complex was observed well selective catalytic properties for the oxidation of cyclohexane to cyclohexanol and cyclohexanone.

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1. Introduction

The condensation reactions of primary amines and aliphatic or aromatic aldehydes to form imine type products, called Schiff base ligands, are well known and they comprise a broad area of research in inorganic and organic chemistry. Schiff base ligands are derived from compounds containing a diazo functional group and their metal complexes have increasingly become significant for catalysis reactions based on the synthesis of organic compounds due to their improved chemical and physical properties [1–5]. Diazonium salts with the general formula of $\text{R-N}_2^+\text{X}^-$ (R: alkyl or aryl; X: inorganic or organic anion) have been generated with the reaction of aryl amines and nitrous acid at a temperature of 0–5 °C. Diazo compounds have been coupled with aryl-aldehydes under convenient reaction conditions. These azo-aldehydes can be converted to primary amines (e.g. 3-aminopropyltriethoxysilane), attached to activated silica-gel (SiO_2APTES). The new silica-supported multifunctional azo-containing Schiff base ligands loaded with different metal ions are useful for obtaining solid phase anchored heterogeneous catalysts due to their wide use in catalytic applications [6–8].

In the recent past, researchers have extensively focused on investigating heterogeneous catalytic reactions. A polymer that includes a polymeric backbone and a transition metal complex possesses the advantages of both high selectivity and easy separation

from the oxidation reaction medium [6–15]. The catalytic effects of the polymer anchored azo-containing complexes demonstrate quite strong stability. Additionally, they can be used under various reaction conditions, such as the presence of moisture and high temperatures [9–12]. In the literature, many of the polymer-supported metal complexes can be used as a catalyst and they exhibit excellent catalytic performance at the hydrogenation and oxidation of the various organic substrates [4,8,9,12,14,15]. Moreover, silica gel, as a mesoporous solid, has been extensively studied due to its catalytic, analytical, optical and electronic properties [4–9,12,14,15]. Activated silica is easily synthesized binding an active compound such as 3-aminopropyltriethoxysilane (APTES) [5–8,12,14–21].

Cyclohexanol (Cy-OH) and cyclohexanone (Cy=O), which are synthesized by the oxidation reaction of cyclohexane (CyH), are used as intermediates for pharmaceuticals, plasticizers, rubber chemicals, cyclohexylamine, pesticides and other organic compounds [22]. For example, cyclohexanol derivative is used as an intermediate for pharmaceuticals to treat diabetes and other diseases related to glucose secretion due to its pharmacological activity. Cyclohexane derivatives are also used in solvents, oil extractants, paints and varnish removers, dry cleaning materials, and solid fuels. Each year, over one million tones of cyclohexanone and cyclohexanol are produced and are usually used for the synthesis of Nylon-6 and Nylon-6,6. Carvalho et al. [25] have worked the cyclohexane oxidation under microwave conditions by using Fe (III) complex catalysts, hydrogen peroxide as an oxidant and

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acetonitrile as a solvent, and Cy–OH, Cy=O and adipic acid were obtained as major products with a good CyH conversion and Cy–OH and Cy=O selectivity. In recent progress on catalysis, the metal-complexes have shown good catalytic activities with good selectivity for the oxidation of cyclohexane and cyclohexene with H₂O₂ oxidant under microwave irradiation [23–25].

In this work, we have prepared a novel azo-containing solid phase, silica-supported Schiff base ligand and its four metals complexes: Cu(II), Ni(II), Co(II), and Mn(II). NMR, FT-MIR/FIR, elemental analysis, ICP-OES, TGA and a scanning electron microscope (SEM) were used for the characterisation of the ligand and its metal complexes. In this study, the synthesis of heterogeneous four L¹–Cu(II)/Co(II)/Mn(II)/Ni catalysts and their catalytic activities in the oxidation of cyclohexane to cyclohexanol and cyclohexanone were reported. Furthermore, the recovery, reusability and, finally, the recyclability of these novel catalysts were investigated under the same reaction conditions.

2. Experimental

2.1. General

All the reagents and organic solvents were purchased from commercial sources and used as received, unless noted otherwise. The NMR spectra were recorded at 25 °C in DMSO-d₆ and CDCl₃ using a Bruker 400 MHz Ultrashield TM NMR spectrometer. The FT-MIR and FAR spectra were obtained using a Perkin Elmer Spectrum 400 FT-IR system in the range of 4000–30 cm⁻¹. Elemental analysis was performed using an LECO CHNS 932 instrument. The metal contents were determined using Perkin Elmer Optima 2100 DV ICP-OES. A JEOL NeoScope Benchtop scanning electron microscope (SEM) was used to scan the images. The thermal analysis studies of the complexes were performed on a PerkinElmer Pyris Diamond DTA/TG thermal system under nitrogen atmosphere at a heating rate of 10 °C/min in the range of 30–900 °C. Kieselgel gel 60 (Merck) silica, having a particle size of 0.2–0.5 mm, was used as solid support for the heterogeneous catalysts. The microwave experiments, which were conducted in closed DAP60 vessels, were carried out in a Berghof MWS-3+ (Germany) equipped with pressure and temperature control. The synthesized products were characterized and analyzed by using a Perkin Elmer Clarus 600 GC (USA) spectrometer equipped with an MS detector fitted with an Elite-5 MS and FID detector fitted with BPX5 capillary columns.

2.2. Preparation of 2-hydroxy-5-((2-methoxyphenyl)diazonyl)benzaldehyde (HMDB:L)

Next, 2-methoxyaniline (o-Anisidine) (0.9852 g, 8 mmol) was mixed with 10 mL NaNO₂ solution (0.6210 g, 9 mmol), then HCl (37%) was added until the pH reached 2. The mixture was stirred for 30 min. Salicylaldehyde (2-hydroxybenzaldehyde) (0.9770 g, 8 mmol) was dissolved in 20 mL pH:12 buffer solution containing NaOH (20 mmol) and Na₂CO₃ (40 mmol). The diazonium solution was added very slowly to the salicylaldehyde solution. While adding, the temperature was kept at 0–2 °C and the pH was kept at around 7–8. The reaction mixture was stirred in the ice bath for 2 h. All the reaction steps were carried out in an ice-water-salt bath at a temperature ranging from 0 to 2 °C. The dark orange product was filtered and recrystallized in EtOH:H₂O (1:1). Several portions of diethyl ether were used to remove the organic impurities from the product. Then the product was dried under vacuum at 60 °C for 12 h. Yield 2.053 g (78%). [C₁₄H₁₂N₂O₃]: calcd C 65.62, H 4.72, N 10.93%; anal. C 65.38, H 4.64, N 10.43%. ¹H NMR (DMSO-d₆, 25 °C): δ 10.38 [s, 1H, CHO], 8.05 and 8.12 ppm [d, 2H, Ar–H(o-/p-)], 7.5 ppm [d, 2H, Ar–H(o-/m-)], 7.19 and 7.05 ppm [t, 2H, Ar–H(m-/p-)], 7.0 ppm [s, 1H, Ar–H(o-)], 3.96 [s, 3H, Ar–C–OCH₃],

3.57 ppm [s, 2H, OH₂]. ¹³C NMR (DMSO-d₆, 25 °C): δ 191.1 [CHO], 163.9 [Ar–C–OH], 156.9 [Ar–C–OCH₃], 145.8, 141.78 [Ar–C–N–], 133.0–113.8 [Ph–C], 56.4 ppm [O–CH₃]. FT-IR (ν, cm⁻¹): 3538–3173 (w, Ar–OH); 2968 (w, Ar–H); 2941 (w, R–H), 1652 (s, C=O), 1591–1581 (s–sh, Ar–C=C), 1487 (s, –N=N–), 1023 (br, C–H); 1023–1043 (s–sh, C–OH), 892 (m, Ar–H). TG/DTA Data: No weight loss was observed below decomposition temperature. Decomposition began at 155 °C and two endothermic peaks were between 155–305 °C (82.79% loss) and 305–805 °C (12.97% loss).

2.3. Preparation of silica-supported 3-aminopropyltriethoxysilane (SiO₂-APTES)

The silica gel (50 g) was refluxed with an excess amount of hydrochloric acid (6 M) for 8 h, then filtered off and washed with an appropriate amount of deionized water until the filtrate was neutral. Activated silica was dried at 150 °C for 12 h. Then, 20 g of activated silica was suspended in 100 mL toluene, and 20 mL 3-aminopropyltriethoxysilane (APTES) was added to the suspension. The reaction mixture was refluxed for 72 h. The suspension was filtered and the filtered solid was washed with an excess amount of toluene, ethanol and diethyl ether, respectively [5,7,8,12,14–20]. Elemental Anal.: C, 8.97; H, 2.32; N, 3.3941%. FT-IR (ν, cm⁻¹): 3696–3319 (br, Si–OH); 3319–3118 (br, –NH₂), 2941 (w, R–H); 1056 (br, Si–O). TG/DTA Data: % 3.37 water or solvent loss was observed between 30 and 155 °C. Decomposition began at 155 °C and continued to 900 °C as one endothermic peak with a 8.64% loss.

2.4. Preparation of silica-supported azo containing Schiff base (SiO₂-APTES-HMDB: L¹)

5 g. SiO₂-APTES was added to HMDB:L (1.28 g, 5 mmol) solution in 100 mL EtOH (96%) and then was refluxed at 60 °C for 12 h. The brown solid was filtered, washed with excess amount of EtOH and dried at 95 °C for 12 h. Elemental Anal.: C, 15.08; H, 2.37; N, 2.47%. FT-IR (ν, cm⁻¹): 3660–3186 (br, –OH); 2957 (w, Ar–H); 2941 (w, R–H), 1622 (s, CH=N), 1487 (s, –N=N–), 1055 (br, Si–O). TG/DTA Data: No weight loss was observed below decomposition temperature. Decomposition began at 180 °C and two endothermic peaks were between 180 and 380 °C (6.70% loss) and 380–900 °C (12.83% loss).

2.5. Preparation of the complexes

Four metal complexes were synthesized by the addition of 1 mmol metal salts (anhydrous CuCl₂, CoCl₂·6H₂O, NiCl₂·6H₂O and Mn(OAc)₂) to the 2 g silica-supported Schiff base ligand (L¹: MDPMP) in EtOH. The mixture was refluxed for 24 h at 50 °C. After stirring, the complexes were filtered and washed with excess amount of water, finally dried in vacuum at 70 °C. Elemental analysis (C, H, N %), ICP-OES (Metal % content after microwave digestion), FT-MIR/FIR, TGA and SEM techniques were used for the characterization of the complexes.

2.6. Preparation of ICP-OES Samples

The complexes were prepared in a Berghof MWS-3+ microwave before the ICP analyses were conducted. A suitable amount of the sample, HNO₃ and HCl, was added to the DAP60 vessel and suitable oven conditions were applied (pressure, temperature and microwave power). The digested suspensions were filtered and diluted with an appropriate amount of ultra-pure water. Consequently, Sample solutions were analyzed by inductively coupled plasma/optical emission spectrometry (ICP/OES) to determine metal content (Co, Cu, Ni, Mn).

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