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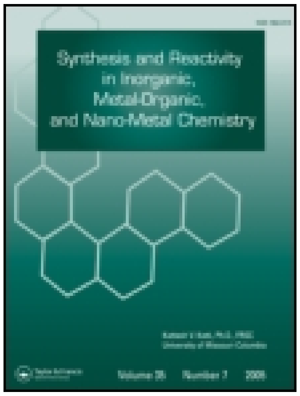

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Chemically Modified Silica-Gel With an Azo-Schiff Ligand and Its Metal Complexes With Cu(II), Co(II), Ni(II) and Mn(II): Applications as Catalysts on the Oxidation of Cyclohexane Under Microwave Power

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Chemically Modified Silica-Gel With an Azo-Schiff Ligand and Its Metal Complexes With Cu(II), Co(II), Ni(II) and Mn(II): Applications as Catalysts on the Oxidation of Cyclohexane Under Microwave Power

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A novel 2-hydroxy-5-((2-hydroxyphenyl)diazenyl)benzaldehyde (L^1: HPDB) ligand was synthesized and bound to silica gel, which was activated with 3-aminopropyltriethoxysilane. Cu(II), Co(II), Ni(II), and Mn(II) complexes of silica-supported ligand (L^2: MDPMP) were synthesized. A buffer (pH = 12) was used for a coupling reaction of diazonium electrophile to salicylaldehyde. The ligand and its complexes were characterized by using NMR, FT-MIR/FAR, elemental analysis, ICP-OES, TGA, and scanning electron microscopy. Catalytic properties of the complexes were investigated for the selective oxidation of cyclohexane under microwave power. Silica-supported L^2-Cu(II) complex showed well selective catalytic activity for the oxidation of cyclohexane to cyclohexanol and cyclohexanone with 8.40% and 3.77% yields with 48.43% conversion.

Keywords azo ligand, catalysis, cyclohexane, oxidation, silica-supported, Schiff base

INTRODUCTION

Diazonium salts are the compounds that are shown as R-$N_2^+X^-$ general formula (R: alkyl or aryl; X: inorganic or organic anion). Diazonium salts are obtained with the reaction of arylamines and nitrous acid at the temperature of 0–5°C. Diazonium compounds can be bound to aromatic rings with electrophilic substitution reaction.[1–3] Reactions between primary amines and aldehydes form the products called as Schiff base ligands that comprise a huge area in inorganic and organic chemistry. Functionalized Schiff base ligands and their metal complexes have increasingly become important in catalytic synthesis of organic compounds because of their improved chemical and physical properties.[4–8] Aryl-aldehydes coupled with diazo compounds can be bound to silica gel activated with a primary amine such as 3-aminopropyltriethoxysilane forming silica-supported azo-Schiff bases. Silica-supported azo-Schiff base ligands can be loaded with different metal ions.[1–3]

The studies on heterogeneous catalysis have replaced with homogeneous catalysis studies due to the fact that the polymer-supported metal complexes have high selectivity and they can be separated easily from the reaction mixture in the oxidation of organic compounds.[6–15] Besides, the catalytic activities of polymer-supported azo complexes are stable even if in the presence of moisture and in high-temperature reactions.[9,10–12] There are numerous metal-azo-Schiff base complexes that are supported and some polymers exhibit excellent catalytic activities in oxidation and hydrogenation of various organic substrates.[4,8,9,12,14,15]

There are two different approaches to support a complex to a solid. One is the use of organic polymeric solids such as polystyrene, another is through inorganic supports such as silica gel or alumina. Mesoporous solids such as silica gel have been extensively studied because of their catalytic, analytical, optical, and electronic properties.[4–9,12,14,15] Activated silica is synthesized binding an active compound such as 3-aminopropyltriethoxysilane (APTES).[5–8,12,14–21]

Cyclohexane (CyH) and its derivatives such as cyclohexanol (Cy-OH) and cyclohexanone (Cy=O) are used as starting compounds in medicine and in the chemical industry. Cy-OH

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and Cy=O are obtained from CyH are used as intermediates for pharmaceuticals, plasticizers, rubber chemicals, cyclohexylamine, pesticides, and other organic compounds. For example, cyclohexanol esters are pharmacologically active compounds and therefore be used as pharmaceuticals, in particular for treating diabetes and other diseases related to glucose secretion. This azo-aldehyde ligand was prepared by modifying the process of the literature.[25] Besides, cyclohexane derivatives are also used as solvents, oil extractants, paints and varnish remover, dry cleaning material, and in solid fuels. More than 1 billion tons of cyclohexanone (Cy=O) and cyclohexanol (Cy-OH) are produced each year and are generally used for the synthesis of Nylon-6 and Nylon-6,6.[22–24] Conaphthenate complex was used as a catalyst to initiate the radicalic oxidation of cyclohexane using molecular oxygen from the air with the conditions that the temperature is 160°C and the pressure is 15 bar. After completed the reaction, only 4% of cyclohexane (CyH) was converted to oxidized products and with selectivity towards Cy=O and Cy-OH. Microwave technology using green oxidant hydrogen peroxide can reduce the reaction times and energy consumption with an increase cyclohexane and cyclohexene conversions and the selectivity of the desired products.[23,24] Carvalho et al.[24] studied the cyclohexane oxidation under microwave conditions by using Fe(III) complex catalysts, hydrogen peroxide as oxidant, and acetonitrile as solvent, and Cy-OH, Cy=O, and adipic acid were obtained as major products with a good CyH conversion and Cy-OH, Cy=O selectivity. In the literature, the metal complexes showed good catalytic activities with good selectivities for the oxidation of cyclohexane and cyclohexene with H_2O_2 oxidant under microwave power.[23,24]

EXPERIMENTAL

General

All 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-d_6 and $CDCl_3$ using a Bruker 400 MHz Ultrashield TM NMR spectrometer. FT-MIR and FAR spectra were obtained by using Perkin-Elmer Spectrum 400 FT-IR system in the range 4000–30 cm^{-1}. Elemental analyses were performed using LECO CHNS 932 instrument. Metal contents were determined by Perkin-Elmer Optima 2100 DV ICP-OES. A Jeol Neoscope Benchtop scanning electron microscope was used for scanning electron microscopy (SEM) images. The thermal analyses studies of the complexes were performed on a Perkin-Elmer Pyris Diamond DTA/TG thermal system under nitrogen atmosphere at a heating rate of 10°C /min in the range 30–900°C. Kiesegel gel 60 (Merck) silica having particle size of 0.2–0.5 mm was used as solid support for heterogeneous catalysts. The microwave experiments were carried out in a Berghof MWS3+ (Germany) equipped with pressure and temperature control. Microwave experiments were done in closed DAP60 vessels. The reaction products were characterized and analyzed by using Perkin-Elmer Clarus 600 GC (USA) equipped with MS detector fitted with Elite-5 MS and FID detector fitted with BPX5 capillary columns.

Preparation of 2-hydroxy-5-((2-hydroxyphenyl)diazenyl) benzaldehyde (HPDB) (L^1)

2-aminophenol (0.8630 g, 8 mmol) was mixed with 10 mL $NaNO_2$ solution (0.6210 g, 9 mmol), then dropped HCl (37%) until pH ∼2. The mixture was stirred for 30 min. Salycilaldehyde (2-hydroxybenzaldehyde) (0.9770 g, 8 mmol) was dissolved in 20 mL pH:12 buffer solution containing NaOH (20 mmol) and Na_2CO_3 (40 mmol). Diazonium solution was added very slowly to salycilaldehyde solution. While being added, the temperature was kept at 0–2°C and pH was kept at around 8–9. The reaction mixture was stirred in the ice bath for 2 h. All reaction steps were carried out in an ice-water-salt bath at the temperature 0–2°C. The dark orange product was filtered and recrystallized in EtOH:H_2O (1:1). Several portions of diethyl ether were used to remove organic impurities from the product. Then the product was dried under vacuum at 60°C for 12 h. Yield: 0.350 g (19%). Anal. Calcd. for [$C_{13}H_{10}N_2O_3$]: C 64.46, H 4.16, N 11.56%. Found: C 64.38, H 4.34, N 11.49%. ^{1}H-NMR (DMSO, δ, ppm): 11.37 [s, 1H, C$\underline{H}$O], 7.86–6.92 [m, 7H, Ar-$\underline{H}$], 3.45 [s, 2H, Ar-O$\underline{H}$]. FT-IR (υ, cm^{-1}): 3669–3120 (br, Ar-OH); 3063 (w, Ar-H); 2927 (w, R-H), 2854 (w, CHO), 1613 (s, C = O), 1581(s, Ar-C = C), 1463 (s, -N = N-), 1109 (w, C-H); 1031 (w, C-OH), 751 (s, Ar-H). TG/DTA Data: No water or solvent loss was observed below decomposition temperature. Decomposition began at 150°C and continued to 900°C as three endothermic peaks with a 95.8% loss.

Preparation of Silica-Supported 3-Aminopropyltriethoxysilane (SiO_2-APTES)

Silica gel (50 g) was refluxed with excess amount of 1:1 hydrochloric acid for 6 h, then filtered off and washed with appropriate amount of deionized water until filtrate was neutral. Activated silica was dried at 150°C for 12 h. Then, 20 g 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 excess amount of toluene, ethanol and diethyl ether, respectively.[5,7,8,12,14–20] Elemental Analysis: C 8.97, H 2.32, N 3.39%. FT-IR (υ, cm^{-1}): 3696–3319 (br, Si-OH); 3319–3118 (br, -NH_2), 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.

Preparation of Silica-Supported Azo Containing Schiff Base (SiO_2-APTES-HPDB: L^2)

5 g SiO_2-APTES was added to HPDB (1.21 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. Yield: 65%. Anal.

Calcd.: C 15.39, H 2.11, N 2.01%. Found: C 15.08, H 2.37, N 2.47%. FT-IR (υ, cm^{-1}): 3665–3098 (br, -OH); 2957 (w, Ar-H); 2930 (w, R-H), 1640 (s, CH = N), 1490 (s, -N = N-), 1050 (br, Si-O). TG/DTA Data: 0.68% water or solvent loss was observed between 30 and 180°C. Decomposition began at 180°C and continued to 900°C as one endothermic peak with a 27.33% loss.

Preparation of the Complexes

Silica-supported complexes of L^2 were synthesized by the addition of 1 mmol metal salts (anhydrous $CuCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $Mn(OAc)_2$) to the 2 g ligand-grafted silica in EtOH. The mixture was refluxed for 24 h at 50°C (pH 7–8). After stirring, the complexes were filtered and washed with excess amount of water and finally dried in vacuum at 70°C. Elemental analysis (C, H, N%), ICP-OES (Metal% content after microwave digestion), FT-MIR/FAR, TGA, and SEM techniques were used for the characterization of the complexes.

Catalytic Oxidation of Cyclohexane under Microwave Irradiation

The catalytic oxidation of cyclohexane under microwave irradiation was performed as follows: 0.02 mmol synthesized complex, 2 mmol cyclohexane (Carlo Erba, 99.8%), and 4 mmol H_2O_2 (Merck, 35%) were microwaved for 75 min at 400 W (40% of maximum output power). The catalyst:substrate:oxidant ratio was of 1:100:200. The complexes were individually suspended in 5 mL acetonitrile, and cyclohexane and H_2O_2 were added in the microwave vessels, respectively, for each oxidation experiments. The vessels were rapidly closed with their captures and the caps and placed inside the Berghof MWS3+ microwave oven. For each catalytic oxidation experiment, 400 W microwave power was applied for 75 min. The temperature was controlled automatically by the microwave instrument at about 110°C, however, sometimes it increased to 130–140°C in a short time during the reaction in the microwave oven and the pressure also increased to 30–35 bar due to the evaporation of solvent. In order to stop the oxidation before analysis, 1 mL H_2O was added in the vessels. The oxidized organic products except organic acids were extracted with 10 mL CH_2Cl_2 and injected to GC and GC-MS to analyze and characterize. CyH, Cy-OH, and Cy=O amounts were calculated from external calibration curves that were prepared before analyses.

RESULTS AND DISCUSSION

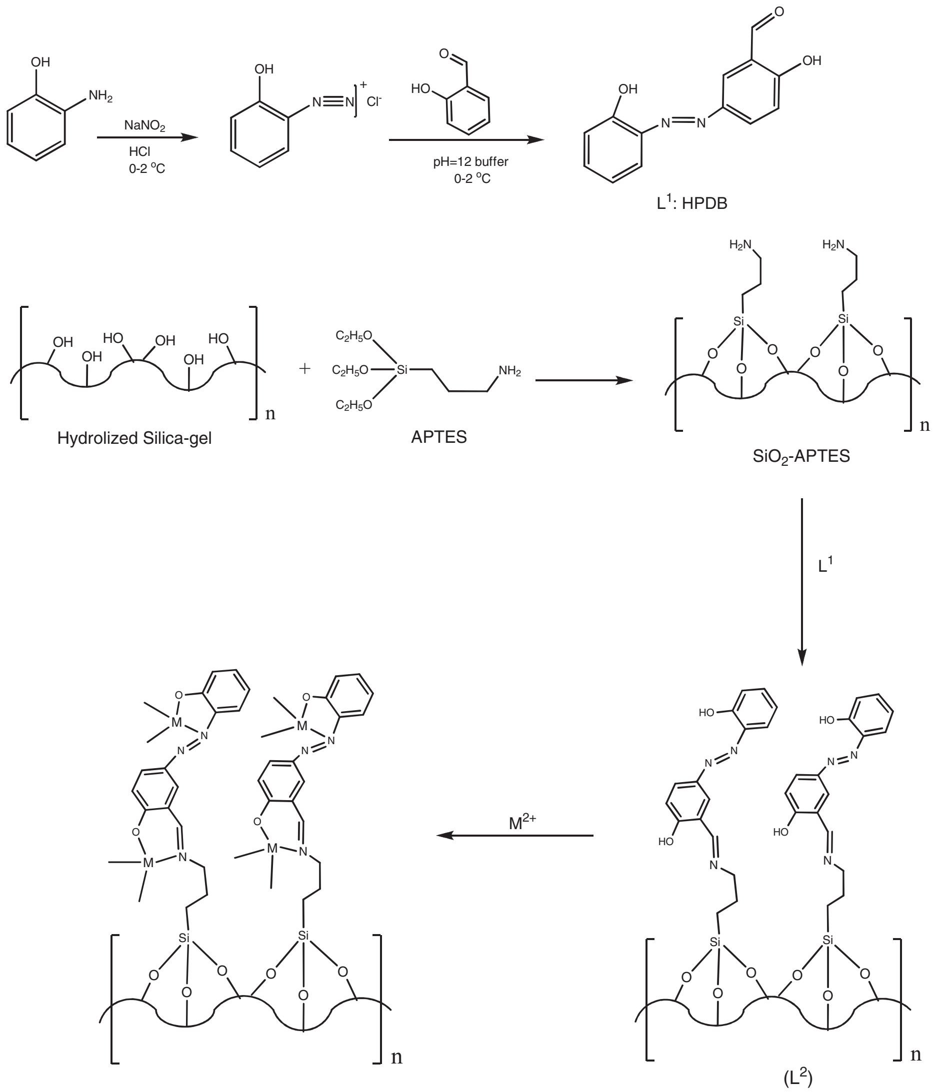
Preparation of Silica-Supported Ligand and Complexes

A novel silica-supported ligand [SiO_2-APTES-HPDB] (L^2) was synthesized using a novel ligand [HPDB] (L^1) and activated silica [SiO_2-APTES] [5,7,12]. Different reaction parameters (pH, temperature, time) were tested in order to determine optimum coupling conditions for the synthesis of L^1, however, maximum 19% yield was obtained when used pH 12 buffer in salicylaldehyde solution. According to our results, when pH is lower than 8–9, coupling does not form. The metal complexes, $[Cu_2(L^2)(H_2O)_2Cl_2]$ (**3**), $[Co_2(L^2)(H_2O)_2Cl_2]$ (**4**), $[Ni_2(L^2)(H_2O)_2Cl_2]$ (**5**), and $[Mn_2(L^2)(OAc)_2(H_2O)_2]$ (**6**) were prepared using anhydrous $CuCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $Mn(OAc)_2$ salts. The chemical structures of L^1 and L^2 and possible structures of the L^2-metal complexes are shown in Scheme 1. The colors of L^2 and their complexes have brown tones.

The functional groups of the synthesized ligands and their complexes were assigned by infrared spectra shown in Figures 1 and 2. Ar-OH, Ar-H, and R-H absorptions for ligand L^1 (a) were observed at about 3669–3120 cm^{-1}, 3063 cm^{-1}, and 2927 cm^{-1}, respectively. A –N = N– stretch was assigned at 1463 cm^{-1}. In the spectrum of SiO_2-APTES showed a broad band in the range 3696–3319 cm^{-1} and at 1056 cm^{-1} can be attributed to silanol-OH groups stretches and Si-O-Si bonds, respectively.[5–8,11–13] The continuing band between 3319 and 3118 cm^{-1} is the stretch of $–NH_2$ groups of silica-supported APTES. Aliphatic $–CH_2$ vibrations can be attributed at 2941 cm^{-1} in the SiO_2-APTES spectrum. Absorbance band of –OH groups of L^1 begins at 3669 cm^{-1} continues to the beginning of the aliphatic and aromatic vibrations at around 2958 cm^{-1}. A band belonging to $–NH_2$ groups in the range of 3319–3118 cm^{-1} disappeared when L^1 bound to SiO_2-APTES (Figure 1). Nevertheless, –CH = N– stretch of L^2 was observed at 1640 cm^{-1} as a strong band in the spectrum. This band prove the Schiff base reaction of the carbonyl groups with $-NH_2$ groups of SiO_2-APTES.[5,7–9,11–13] The FT-IR spectra of the silica-supported complexes showed significant differences from the silica-supported ligand L^2. However, when the metal ions coordinated to L^2, –CH = N– stretching frequencies slightly shifted to lower frequencies (1635 cm^{-1}).[5,7–9,11–13] Additionally, –N = N– frequencies of the complexes were shifted to about 1506 cm^{-1}. These results show that L^2 coordinates to metal ion with two side of it, one is –CH = N–, –OH groups and other is –N = N–, –OH groups[5,11,12]. New M-O and M-N absorption bands in the FAR spectra were observed at about 462 cm^{-1} and 543 cm^{-1}, respectively (Table 1). In FT-IR spectrum of $[Mn(L^2)(OAc)(H_2O)]$, the new C = O stretch of acetate ligand was observed at 1646 cm^{-1} (Figure 2). The new M-X (X: Cl^- for Cu(II), Co(II), and Ni(II) complexes, OAc^- for Mn(II) complex) stretches were at about 366 cm^{-1} in FAR spectra. Coordinations of halides or acetate in the complexes were characterized further with qualitative methods such as argentometric method for halide coordination.[5,9,11,12]

^1H-NMR spectrum of L^1 was recorded by using DMSO-d_6 as solvent. The singlet peak of aldehyde hydrogen of L1 was observed at 11.37 ppm. The aromatic protons (7H) gave a multiple signal at 7.86–6.92 ppm. The singlet signal of aromatic –OH protons were recorded at 3.45 ppm. These ^1H-NMR data confirm the chemical structure of synthesized ligand:[5,7–13]

Elemental analysis techniques (C, H, N, and metal%) were used for further characterization of the ligands and their complexes. Silica-supported ligand have 1 mmol ligand:1 g silica ratio. According to the increase of weight of activated silica



SCH. 1. Synthesis of L^1, L^2 and the possible coordination of metals to L^2. M^{2+} : Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}

gel, nearly 65% of ligand bound to activated silica gel. While C and H percentages increase, N percentage decreased after binding L^1 to SiO$_2$-APTES. These differences confirm supporting L^1 to SiO$_2$-APTES and Schiff base forming. Metal content of the complexes were also determined by using ICP-OES. Before ICP analyses, silica-supported complexes were digested with the Berghof MWS3+ microwave. Approximately 0.25 g sample was added in DAP60 vessel and 2 mL HNO$_3$ and 3 mL HCl placed into this vessel. After waiting 5 min, vessels were closed with their capture and caps and a suitable program (pressure, temperature, and microwave power) were applied. Digested solutions were filtered and diluted appropriate amount of ultrapure water. According to the metal analyses results, metal absorption capability of the silica-supported ligand (L^2) is good enough and L^2:M ratio is 1:2 (Table 1).

The SEM images of SiO$_2$-APTES, L^2 and the complexes of L^2 are shown in Figure 3. The morphological differences between silica gel and the complexes in SEM images are very important evidence of the loading of the complexes both on to the SiO$_2$ particles and cavities of it as clusters. When L^1, which diffuses through the SiO$_2$ channels, reacts with metal ions, it is obtained well dispersed complexes through SiO$_2$ channels and over SiO$_2$ particles. Well-dispersed silica-supported Cu-L^2 complex showed a good catalytic activity as a result of having a huge surface on the silica particles and its cavities as an internal and external surface as seen in Figure 3.[6,9,12,13,15]

Thermal behavior of the ligands and the complexes were investigated by using thermogravimetry (TG). TG curves of the ligands and the complexes are shown in Figure 4.

While the ligand (L^2) has two mass loss peaks in TG curves, the complexes show three mass loss peaks. The silica-supported ligand (L^2) has a water or solvent loss peak (0.68% loss) between 30 and 180°C and decomposition starts at 180°C in TG curves (27.33% loss). When combined the results of the

TABLE 1

Chemical composition and characteristic MIR and FAR peaks of the ligands and the complexes

Compound	C %	H %	N %	Metal loading (mmol.g^{-1})	Metal analysis[a] (mmol.g^{-1})	υ_{OH}	$\upsilon_{Ar\text{-}H}$	$\upsilon_{R\text{-}H}$	$\upsilon_{CH=N}$	$\upsilon_{N=N}$	$\upsilon_{Si\text{-}O}$	$\upsilon_{M\text{-}N}$	$\upsilon_{M\text{-}O}$	$\upsilon_{M\text{-}X}$
SiO_2-APTES	8.97	2.32	3.39	—	—	3696-3319	—	2941	—	—	1056	—	—	—
L^1	64.38 (64.46)	4.34 (4.16)	11.49 (11.56)	—	—	3669-3120	3063	2927	—	1463	—	—	—	—
L^2	15.08	2.37	2.47	—	—	3665-3098	2957	2930	1640	1490	1050	—	—	—
$[Cu_2(L^2)(H_2O)_2Cl_2]$	14.50	2.22	2.03	0.5	0.44	3618-3100	2957	2930	1635	1506	1051	542	462	365
$[Co_2(L^2)(H_2O)_2Cl_2]$	12.50	2.22	2.12	0.5	0.49	3619-3099	2958	2931	1634	1506	1056	543	462	366
$[Ni_2(L^2)(H_2O)_2Cl_2]$	13.49	2.16	1.85	0.5	0.50	3618-3099	2956	2941	1635	1507	1055	543	462	366
$[Mn_2(L^2)(OAc)_2(H_2O)_2]$	13.09	2.17	1.85	0.5	0.50	3618-3100	2958	2930	1635	1506	1055	542	463	366

[a] Metal analyses were performed by using ICP-OES. Solid-supported complexes were digested with MWS3+ microwave digestion system. Figure in parentheses indicates the possible calculated value.

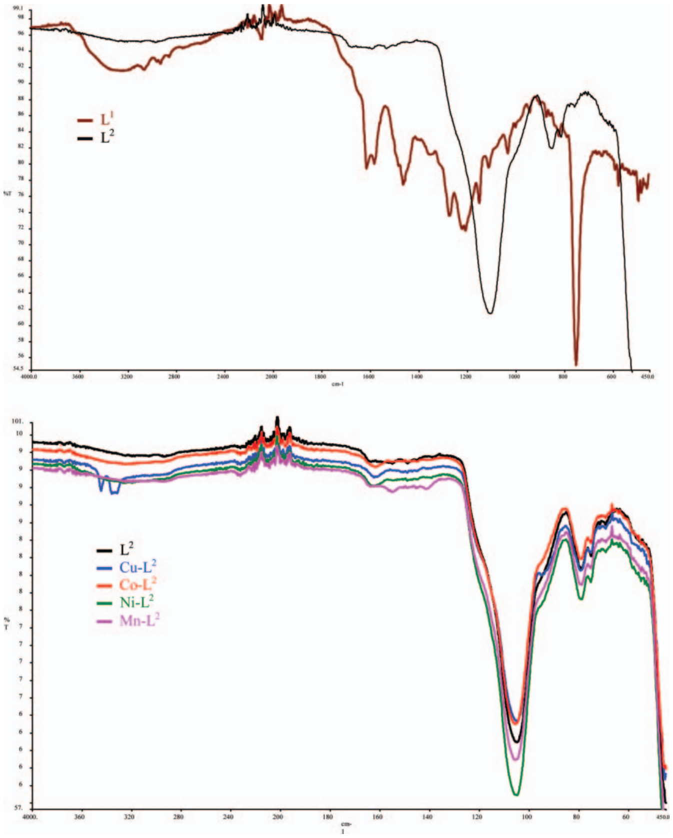


FIG. 1. FT-IR spectra of the ligands and the complexes (color figure available online)

elemental analyses and TG curves, it can be concluded that L^2 has little hydrate or adsorbed/absorbed water. In TG curves of the complexes, two loss as a result of decomposition of the supported ligand and the formation of metal oxides could be detected between about 145–600°C.[5,7–9,12,13] 2.28% loss in the TGA curve of [$Mn(L^2)(OAc)(H_2O)$] complex between 30 and 145°C can be attributed to coordinated water. In addition, an acetate ligand in Mn(II) complex increased the decomposition percentage between 145 and 660°C in the TGA curve (Table 2).

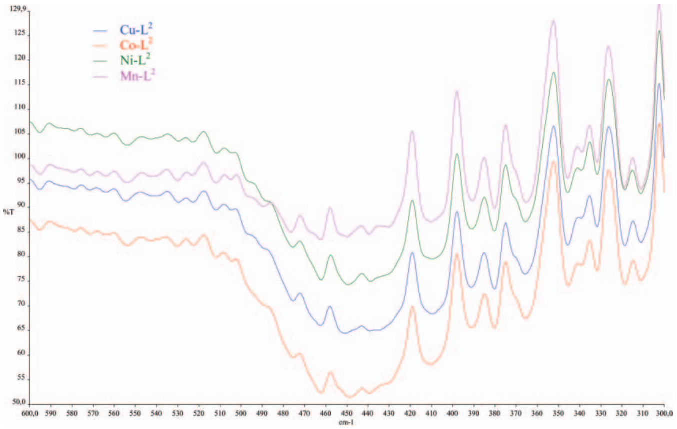


FIG. 2. FT-FAR of the complexes (color figure available online).

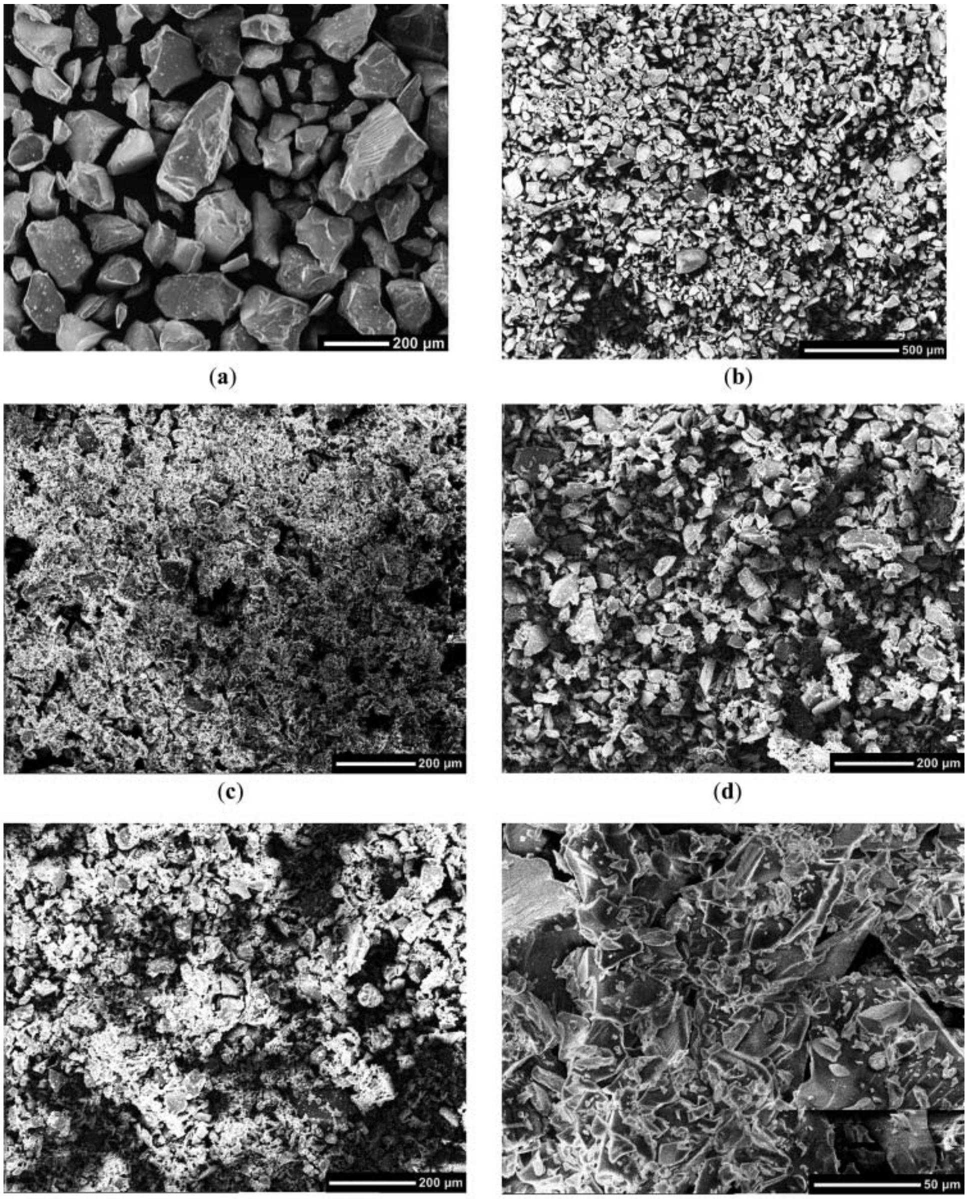
Based on FT-MIR/FAR spectral values, elemental analysis (C, H, N, and M%) and other chemical characterizations, it can be concluded that the complexes are tetracoordinated. Two coordination sites of the metal cations in the complexes have had two halogen ligands and two aqua ligands for each Cu-L^2, Co-L^2, and Ni-L^2 complex and two acetate ligands and two water ligands for the Mn-L^2 complex. Having two active functional regions of the silica-supported ligand L^2 allowed 1:2 ratio for L:M. These probable structures are also accordance with our previous studies and other literatures.[5,7–9,11–13]

Catalytic Oxidation of Cyclohexane Under Microwave Irradiation

According to the possible oxidation mechanism (Figure 5), the first and the slow step is the oxidation of CyH to Cy-OH and after that Cy=O and other further oxidized products

TABLE 2
Thermogravimetric data of the ligand and the complexes

Compounds	TG range (°C)	Mass loss (%)	Assignment
SiO_2-APTES	30–155	3.37	Loss of solvent and water
	155–900	8.64	APTES decomposition
L^2	30–180	0.68	Loss of solvent and water
	180–900	27.33	Ligand decomposition
[$Cu_2(L^2)(H_2O)_2Cl_2$]	30–170	0.17	Loss of solvent and water
	170–540	25.58	Ligand decomposition and metal oxide formation
[$Co_2(L^2)(H_2O)_2Cl_2$]	30–175	0.19	Loss of solvent and water
	175–685	17.47	Ligand decomposition and metal oxide formation
[$Ni_2(L^2)(H_2O)_2Cl_2$]	30–185	2.57	Loss of solvent and water
	185–620	22.37	Ligand decomposition and metal oxide formation
[$Mn_2(L^2)(OAc)_2(H_2O)_2$]	30–145	2.28	Loss of solvent and water
	145–660	24.40	Ligand decomposition and metal oxide formation



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**)

FIG. 3. Scanning electron microscopy images of silica-gel (**a**) and the complexes; $[Cu_2(L^2)(H_2O)_2Cl_2]$ (**b,f**), $[Co_2(L^2)(H_2O)_2Cl_2]$ (**c**), $[Ni_2(L^2)(H_2O)_2Cl_2]$ (**d**), $[Mn_2(L^2)(OAc)_2(H_2O)_2]$ (**e**). (Accelerating voltage: 10 kV, vacuum: high).

arise. If it is controlled the first step of the oxidation reaction, the desired products Cy-OH and Cy=O selectivity can be increased.

The possible reaction products are shown in Figure 6 using H_2O_2 and catalyst under microwave.

It has been proposed that the microwave power and the novel catalysts could affect the selective oxidation of CyH to Cy-OH and Cy=O. Reaction time, oxidant amount, catalyst amount, and microwave oven parameters were tested in order to determine optimum catalytic oxidation parameters under microwave power.[12,13] The optimum oxidation conditions were obtained as a 1:100:200 ratio for catalyst:substrate:oxidant, respectively, in acetonitrile under a 400 W microwave power for 75 min. The temperature and pressure were controlled at about 110°C and 30 bar, respectively, throughout the experiment. These optimum parameters were applied for all catalytic experiments. A blank has been run under the same conditions without any catalyst (Table 3).

The ligands containing N, O atoms, can promote proton-shift.[26] In the present study, synthesized new ligands has N

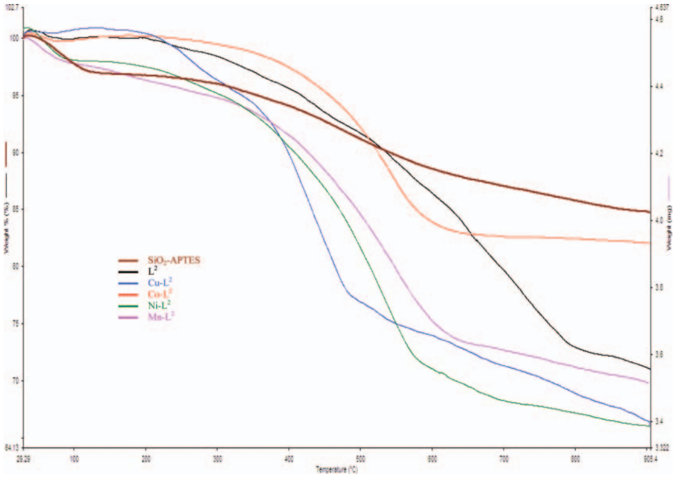


FIG. 4. TG of the silica-supported ligand (L^2) and its complexes (color figure available online).

and O donor atoms. Classical thermal oxidation studies require very long time and control of reaction conditions is very difficult. However, microwave oxidation decreases the reaction time and increases selectivity.[12,13,22,24,27] Hence, microwave power is very usable, easy, and clean for organic and inorganic syntheses. When compared with previous results, in the present study, new synthesized catalysts are not quite effective on the oxidation of cyclohexane. On the other hand, these complexes had good selectivity. It has been shown that Cu(II), Co(II), and Fe(II) complexes of ligands possess catalytic effect. Cy-OH and Cy=O selectivity of Cu(II) catalyst by using microwave power is considerable when compared with the classical oxidation of CyH in the literature.[9,10,12,13,22–27] The best selectivity of the desired products was obtained with silica-supported Cu(II) complex, whereas the products Cy-OH and Cy=O mol percentages are not good (Figure 6). Ni(II) complex has 38.74% cyclohexane conversion, however, selectivity is not good enough because of further oxidized products.

The key point in the conversion of cyclohexane to the oxidized products is the reduction of Cu(II)–L^2 to Cu(I)–L^2. This reduction to Cu(II)–L^2 is facilitated the ligands available around the metal cation. The formation of the oxidation products Cy–OH and Cy=O show the preferential attack of the activated bonds. Tetrahedral geometry of Cu(II) complex may be the reason of the having higher selectivity rather than the other complexes.

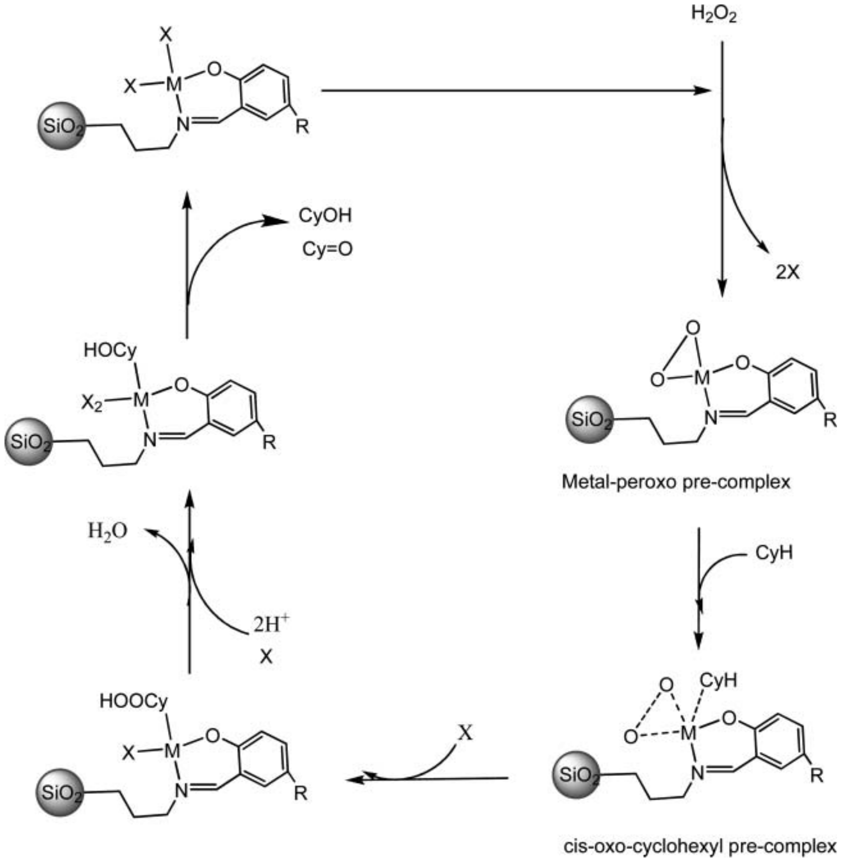


FIG. 5. Possible mechanism of catalytic oxidation of cyclohexane. X: Cl^-, OAc^- or H_2O.

TABLE 3
Catalytic oxidation of cyclohexane (CyH) with H_2O_2 under microwave irradiation[a]

Entry	Catalyst[a]	CyH conversion (mol %)	Desired products (mol %)	ol:one	By-products (mol %)
1[b]	Blank	0.86	Cy-OH (0.54); Cy=O (0.32)	1.72	—
2[c]	$[Cu_2(L^2)(H_2O)_2Cl_2]$	48.43	Cy-OH (8.40); Cy=O (3.77)	2.23	36.26
3[c]	$[Co_2(L^2)(H_2O)_2Cl_2]$	6.45	Cy-OH (0.48); Cy=O (0.06)	8.00	5.91
4[c]	$[Ni_2(L^2)(H_2O)_2Cl_2]$	38.74	Cy-OH (2.95); Cy=O (7.15)	0.41	28.64
5[c]	$[Mn_2(L^2)(OAc)_2(H_2O)_2]$	7.24	Cy-OH (0.54); Cy=O (0.51)	1.06	6.19

[a] 400 W power was applied for 75 min. The reaction temperature and pressure were held at around 110°C and 30 bar in closed DAP60 vessels. [b] 2 mmol cyclohexane:4 mmol hydrogen peroxide and 5 mL acetonitrile were used in experiment without catalyst. [c] 0.02 mmol catalyst:2 mmol cyclohexane:4 mmol hydrogen peroxide (1:100:200) and 5 mL acetonitrile were used for each reaction.

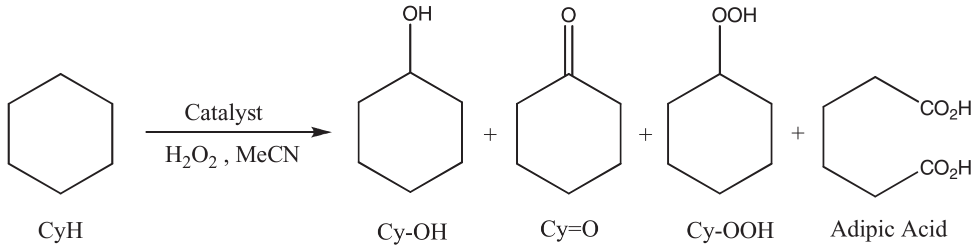


FIG. 6. Catalytic oxidation of cyclohexane under microwave irradiation[12].

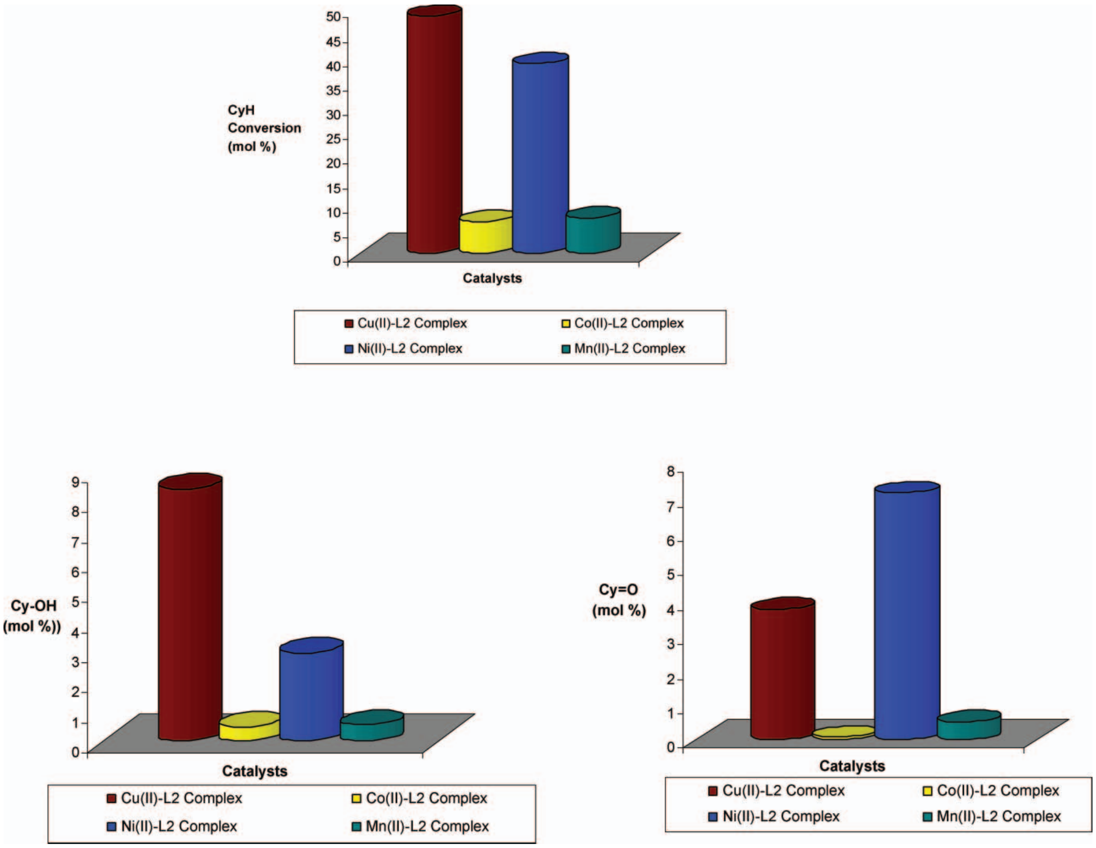


FIG. 7. Influence of the complexes in cyclohexane oxidation under microwave irradiation. 0.02 mmol complex:2 mmol cyclohexane:4 mmol hydrogene peroxide (1:100:200) and 5 mL acetonitrile were used for each reaction.400 watt power were applied for 75 min. The reaction temperature and pressure were held at around 110–140°C and 30 bar in closed DAP60 vessels (color figure available online).

CONCLUSION

In the present study, the novel silica-supported azo-containing Schiff base and its Cu(II), Co(II), Ni(II), and Mn(II) complexes were synthesized. The used characterization techniques have approved the possible structure of the ligand and the complexes. The clean and green oxidation of cyclohexane to cyclohexanol and cyclohexanone under microwave irradiation using H_2O_2 was also investigated using silica-supported Cu(II), Co(II), Ni(II), and Mn(II) complexes. The results showed that the Cu-complex was more selective catalyst for the oxidation of cyclohexane to cyclohexanol and cyclohexanone when compared with other complexes.

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