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

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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  $R-N_2^+X^-$  (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<sub>2</sub>APTES). 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

#### ABSTRACT

In this paper, a novel solid phase supported Schiff base ligand (L<sup>1</sup>: 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<sup>1</sup>: MDPMP) were obtained. The ligand and its four metal complexes were characterized by using NMR (<sup>1</sup>H and <sup>13</sup>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<sup>1</sup>-Cu (II) complex was observed well selective catalytic properties for the oxidation of cyclohexane to cyclohexanol and cyclohexanone. © 2014 Elsevier B.V. All rights reserved.

> 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  $H_2O_2$  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  $L^1$ -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-d<sub>6</sub> and CDCl<sub>3</sub> 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<sup>-1</sup>. 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)diazenyl)benzaldehyde (HMDB:L)

Next, 2-methoxyaniline (o-Anisidine) (0.9852 g, 8 mmol) was mixed with 10 mL NaNO<sub>2</sub> 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 Na<sub>2</sub>CO<sub>3</sub> (40 mmol). The diazonium solution was added very slowly to the salicylaldehyde solution. While adding, the temperature was kept at 0–2  $^\circ C$  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:H<sub>2</sub>O (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%). [C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>]: calcd C 65.62, H 4.72, N 10.93%; anal. C 65.38, H 4.64, N 10.43%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 25 °C): 8 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-OCH<sub>3</sub>],

3.57 ppm [s, 2H,  $OH_2$ ]. <sup>13</sup>C NMR (DMSO- $d_6$ , 25 °C):  $\delta$  191.1 [CHO], 163.9 [Ar–C–OH], 156.9 [Ar–C–OCH<sub>3</sub>], 145.8, 141.78 [Ar–C–N–], 133.0–113.8 [Ph–C], 56.4 ppm [O–CH<sub>3</sub>]. FT–IR ( $\nu$ , cm<sup>-1</sup>): 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 (SiO<sub>2</sub>-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 ( $\nu$ , cm<sup>-1</sup>): 3696–3319 (br, Si–OH); 3319–3118 (br, –NH<sub>2</sub>), 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 (SiO<sub>2</sub>-APTES-HMDB: $L^1$ )

5 g. SiO<sub>2</sub>-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 ( $\nu$ , cm<sup>-1</sup>): 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 CuCl<sub>2</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O and Mn(OAc)<sub>2</sub>) to the 2 g silica-supported Schiff base ligand (L<sup>1</sup>: 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, HNO<sub>3</sub> 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).

#### 2.7. 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<sub>2</sub>O<sub>2</sub> (Merck, 35%) were microwaved for 75 min at 400 watt (40% of maximum output power). The catalyst:substrate:oxidant ratio was 1:100:200. The complexes were individually suspended in 5 mL of acetonitrile, and cyclohexane and H<sub>2</sub>O<sub>2</sub> were added to the microwave vessels, respectively, for each of the 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 watt microwave power was applied for 75 min. The temperature was controlled automatically by the microwave instrument at about 110 °C: however, sometimes the temperature 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 the solvent. In order to stop the oxidation before analysis, 1 mL H<sub>2</sub>O was added to the vessels. The oxidized organic products were extracted with 10 mL CH<sub>2</sub>Cl<sub>2</sub> and injected into GC and GC-MS for analysis and characterisation. The amount of CyH, Cy-OH, and Cy=O were calculated from the external calibration curves that were prepared before the analyses.

#### 3. Results and discussion

#### 3.1. Preparation of silica-supported ligand and complexes

[SiO<sub>2</sub>-APTES-HMDB] (L<sup>1</sup>) novel Schiff base ligand was synthesized using 2-hydroxy-5-((2-methoxyphenyl)diazenyl) benzaldehyde [HMDB:L] and activated silica [SiO<sub>2</sub>-APTES] according to route in the reported studies [5,7,12]. [Cu (L<sup>1</sup>)(H<sub>2</sub>O)Cl] (**3**), [Co(L<sup>1</sup>)  $(H_2O)Cl]$  (4),  $[Ni(L^1)(H_2O)Cl]$  (5), and  $[Mn(L^1)(OAc)(H_2O)]$  (6) complexes were prepared using anhydrous CuCl<sub>2</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, and Mn(OAc)<sub>2</sub> salts. The chemical structures of L and  $L^1$  and possible structures of the  $L^1$ -metal complexes are shown in Scheme 1. The colors of L<sup>1</sup> and the complexes have brown tones. Synthesized ligands and their complexes were characterized by FT-MIR/FIR infrared spectra, as shown in Figs. 1 and 2. A broad(br) band in the range  $3696-3319 \text{ cm}^{-1}$  and a sharp(sh) peak at 1056 cm<sup>-1</sup> can be attributed to the silanol-OH group stretches and the Si-O-Si bonds, respectively, in the spectrum of SiO<sub>2</sub>-APTES [5-8,11-13]. The sharp band between 3319 and 3118 cm<sup>-1</sup> is the stretch of the -NH<sub>2</sub> group. The aliphatic -CH<sub>2</sub> vibrations can be attributed at 2941 cm<sup>-1</sup>. The absorbance band of the –OH group's band of ligand L<sup>1</sup> begins at 3670 cm<sup>-1</sup>, and finishes at the beginning of the aliphatic and aromatic vibrations at around 2968 cm<sup>-1</sup>. The Ar–OH, Ar–H and R–H absorptions for ligand L (a) were observed at about  $3538-3173 \text{ cm}^{-1}$ ,  $2968 \text{ cm}^{-1}$  and 2941 cm<sup>-1</sup>, respectively. The -N=N- stretch was assigned at 1487 cm<sup>-1</sup>. The -NH<sub>2</sub> band of the SiO<sub>2</sub>-APTES in the range of 3329-2980 disappeared when L was bound to SiO<sub>2</sub>-APTES (Supplementary Fig. S5). Nevertheless, the -CH=N- stretch of  $L^1$  was observed at 1635 cm<sup>-1</sup> as a strong(s) band in the infrared spectra. This band proves the condensation reaction of the carbonyl groups with the -NH<sub>2</sub> groups of SiO<sub>2</sub>-APTES. The FT-IR spectra of the silicasupported complexes show significant differences from the silicasupported ligand L<sup>1</sup>. The -CH=N- stretching frequencies of the complexes were slightly shifted to lower frequencies compared with  $L^1$  (Fig. 1) [5,7–9,11–13]. Due to the fact that the -N=N- frequencies of the complexes did not change, it can be said that the azo-groups have not coordinated to any of the metal cations. When all the characterisation data is combined and evaluated, it can be concluded that the L<sup>1</sup> to the metal ions only coordinated with the -CH=N- and the -OH groups. To the determine the coordination sites that might be involved in chelation, the IR spectra of the metal complexes were compared with the free ligand "L<sup>1</sup>". The intensities of these peaks were observed to be changed upon chelation. The band at around 1635 cm<sup>-1</sup> was assigned to the v(C=N)stretching vibrations of the azomethine of the novel ligand "L1" (Table 1). This band was shifted in range from 13 to  $22 \text{ cm}^{-1}$  a lower wavenumber which showed the participation of the azomethine group of ligand "L<sup>1</sup>" in binding to the meta ions. The coordination of the halides or the acetate in the complexes was investigated further using qualitative methods, such as the argentometric method for halide coordination [5,9,11,12]. The quite weakbands in the two ranges  $(678-536 \text{ cm}^{-1})$  and (586-455 cm<sup>-1</sup>) were related to the stretching frequencies of the v(M-N) and v(M-O) bands demonstrating the attached of H<sub>2</sub>L ligand to the center metal ions through the phenolic oxygen atoms and the azomethine nitrogen, respectively [26]. Herein, new M–O and M-N absorption bands in the FIR spectra were respectively observed at about 449 and 522 cm<sup>-1</sup>, which confirmed that the metal ions bonded to L<sup>1</sup> ligand (Table 1). In addition, the monochloro copper (II), nickel (II) and cobalt (II) complexes exhibited a characteristic frequencies  $v_{M-CI}(M = C (II), Co (II), and Ni (II))$ around 365 cm<sup>-1</sup>(Fig. 2) [27]. In the FT-IR spectrum of  $Mn(L^1)$  $(OAc)(H_2O)$ , the new carbonyl (C=O) stretch of the acetate ligand was observed at 1634  $\text{cm}^{-1}$  (Fig. 2).

The <sup>1</sup>H/<sup>13</sup>C NMR spectra were evaluated for further characterisation of HMDB. The singlet peak of the aldehyde hydrogen of L was observed at 10.38 ppm. The two doublet peaks of L were observed at 8.12 and 8.05 ppm attributed to para- and meta- positions hydrogens of salicylaldehyde. The two doublet peaks of L were observed at 7.5 ppm related to orto- and meta- positions hydrogens of 2-methoxyaniline. The two triplets of L were observed at 7.19 and 7.05 ppm assigned to other hydrogens of 2-methoxyaniline. The singlet peak was also seen at 7.0 related to second orto-position hydrogen of salicylaldehyde. The broad signal due to water in DMSO was recorded at 3.57 ppm. The arylmethoxy protons were recorded at 3.96 ppm as a singlet peak. In order to obtain further information. <sup>13</sup>C NMR shifts were assigned for HMDB:L. The singlet peak of the -CHO carbon was seen at 194.60 ppm. The multiple aromatic carbons' peaks were shown at 163.94 ppm for Ar-C-OH, 156.92 for Ar-C-OCH<sub>3</sub>, 145.80 and 141.80 ppm for Ar–*C*–N=N–*C*–Ar and 133.03–113.84 for the other Ar-carbons. The singlet signal of the aryl-methoxy peak was attributed at 56.42 ppm. These <sup>1</sup>H NMR and <sup>13</sup>C NMR data support the formulation of a synthesized compound "HMDB:L"] [5,7-13].

Elemental analysis techniques (percentages of C, H, N and metal) were also used for further characterisation of the ligands and the complexes. While the C and H percentages increased, the N percentage decreased after binding L to SiO<sub>2</sub>-APTES. These differences confirm the conversion of L to SiO<sub>2</sub>-APTES and Schiff base formation. The metal content of the complexes was also determined using ICP-OES. According to the metal analyses results, the metal absorption capability of the silica-supported ligand (L<sup>1</sup>) is good enough and the L<sup>1</sup>:M ratio is 1:1 (Table 1).

The SEM images of SiO<sub>2</sub>-APTES and the complexes of some metal ions(Co(II), and Ni(II)) are shown in Fig. 3. The morphological differences between the silica gel and the complexes in the SEM images are very important proof of the loading of the complexes, both onto the SiO<sub>2</sub> particles and into the cavities as clusters. When L, which diffuses through the SiO<sub>2</sub> channels, reacts with the metal ions, well-dispersed complexes are obtained through the SiO<sub>2</sub> channels and over the SiO<sub>2</sub> particles. The well-dispersed silica-supported Cu-L<sup>1</sup> complex showed good catalytic activity as a result of having a large surface on the silica particles and also being dispersed into the cavities as part of the internal and external surface clusters, as seen in Fig. 3 [6,9,12,13,15,28].



Scheme 1. Synthesis of HMDB:L,  $L^1$  and the possible coordination of metals to  $L^1$  ( $M^{2+} = Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Mn^{2+}$ ).

Thermal properties of the ligands and the complexes were investigated by using thermogravimetry (TG) (Supplementary Fig. S4).

According to the TGA curves, L did not have water or solvent loss before the decomposition temperature was applied. Two endothermic peaks were formed between 155–305 °C (82.79% loss) and 305–805 °C (12.83% loss). While ligand (L<sup>1</sup>) has two mass loss peaks in the TG curves, the complexes show three mass loss peaks. The silica-supported ligand (L<sup>1</sup>) did not lose any water molecules between 30 and 180 °C and decomposition started at 180 °C and continued to 900 °C in the TG curves. When, the results of the elemental analyses and TG curves are combined, it can be concluded that HMDB(L) and L<sup>1</sup> do not have any hydrated or adsorbed/absorbed water. The main loss, which was decomposition of the supported ligand and the formation of the metal oxides, could be detected between 150–375 °C and 375–800 °C, respectively, in the TG curves of the complexes [5,7–9,12,13]. The 2.28% loss in the TGA curve of the  $Mn(L^1)(OAc)(H_2O)$  complex between 30 and 165 °C can be attributed to the coordinated water. In addition, the acetate ligand in the Mn (II) complex increased the decomposition percentage when the temperature ranged between 165–800°C in the TGA curve (Supplementary Table S1). When the thermogravimetric data is evaluated, it can be said that the thermal properties of the complexes are very similar in character (Table S1).

When the FT-MIR/FIR spectral values, elemental analysis (percentages of C, H, N and metal) and other chemical characterisations are combined, it can be concluded that the complexes are tetracoordinated. Two coordination sites of the metal cations in the complexes had one halogen ligand and one aqua ligand for each  $Cu-L^1$ ,  $Co-L^1$  and  $Ni-L^1$  complex and one acetate ligand and one water ligand for the  $Mn-L^1$  complex. Having a bulk structure of a silica-supported ligand "L<sup>1</sup>" does not allow for a 1:2 ratio for the









| Chemical composition | on and characte | eristic MIR and H | IR peaks of t | he ligands and the com | igands and the complexes.   |  |  |  |  |
|----------------------|-----------------|-------------------|---------------|------------------------|-----------------------------|--|--|--|--|
| Compound             | С %             | Н %               | N %           | Metal loading          | Metal analysis <sup>a</sup> |  |  |  |  |

| Compound                                  | C %           | Н %         | N %           | Metal loading<br>(mmol g <sup>-1</sup> ) | Metal analysis <sup>a</sup><br>(mmol g <sup>-1</sup> ) | v <sub>oH</sub> | $v_{Ar-H}$ | $v_{\rm R-H}$ | v <sub>CH=N</sub> | v <sub>N=N</sub> | v <sub>Si-O</sub> | $v_{M-N}$ | $v_{M-O}$ |
|---|---------------|-------------|---------------|--|--|-----------------|------------|---------------|-------------------|------------------|-------------------|-----------|-----------|
| SiO <sub>2</sub> -APTES                   | 8.97          | 2.32        | 3.39          | -  | _  | 3696-3318       | -          | 2941          | -                 | -                | 1056              | -         | -         |
| L   | 65.38 (65.62) | 4.64 (4.72) | 10.43 (10.93) | -  | -  | 3538-3173       | 2968       | 2941          | -                 | 1487             | -                 | -         | -         |
| $L^1$                                     | 16.32         | 2.40        | 3.65          | -  | -  | 3660-3186       | 2957       | 2941          | 1635              | 1487             | 1055              | -         | -         |
| [Cu(L <sup>1</sup> )(H <sub>2</sub> O)Cl] | 13.77         | 2.28        | 3.18          | 0.50                                     | 0.17   | 3663-3186       | 2958       | 2942          | 1622              | 1487             | 1055              | 522       | 449       |
| $[Co(L^1)(H_2O)Cl]$                       | 13.61         | 2.26        | 3.10          | 0.50                                     | 0.22   | 3662-3186       | 2958       | 2941          | 1613              | 1487             | 1055              | 522       | 449       |
| $[Ni(L^{1})(H_{2}O)Cl]$                   | 12.19         | 2.41        | 2.77          | 0.50                                     | 0.21   | 3661-3186       | 2956       | 2941          | 1615              | 1486             | 1055              | 523       | 450       |
| $[Mn(L^1)(OAc)(H_2O)]$                    | 14.01         | 2.29        | 3.11          | 0.50                                     | 0.23   | 3661-3185       | 2958       | 2941          | 1615              | 1487             | 1055              | 523       | 449       |

<sup>a</sup> Metal Analyses were performed by using ICP-OES. Solid-supported complexes were digested with MWS3+ microwave digestion system. Figure in parenthesis indicates the calculated value.







**(b)** 



(**c**)

Fig. 3. Scanning electron microscopy images of silica-gel (a) and the complexes, [Co(L<sup>1</sup>)(H<sub>2</sub>O)Cl] (b), [Ni(L<sup>1</sup>)(H<sub>2</sub>O)Cl] (c). (Accelerating voltage: 10 kV, vacuum: high).

M:L. These probable structures are in accordance with our previous studies and the findings from other literature [5,7–9,11–13].

#### 3.2. Catalytic oxidation of cyclohexane under microwave irradiation

The first step, which is also the slowest step, is the oxidation of CyH to Cy–OH; after that, Cy=O and other further oxidized products arise, according to the possible oxidation mechanism. If the first step of the oxidation reaction can be controlled, the selectivity of the desired products, Cy–OH and Cy=O, can be increased. The possible reaction mechanism and the possible reaction products are shown in Fig. 4. The catalytic oxidation tests under microwave irradiation were applied according to our previous studies [12,13].

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. The reaction time, oxidant amount, catalyst amount and microwave oven parameters were tested in order to determine the optimum catalytic oxidation parameters under microwave irradiation [12,13]. The optimum oxidation conditions were obtained as follows: a catalyst:substrate:oxidant ratio of 1:100:200 in acetonitrile under 400 watt microwave power for 75 min. The temperature and pressure were controlled at about



Fig. 4. Possible mechanism of catalytic oxidation of cyclohexane (X: Cl<sup>-</sup>, OAc<sup>-</sup> or H<sub>2</sub>O).

110 °C and 30 bar, by the instrument. These optimum parameters were applied in all the catalytic experiments. A control group has been run under the same conditions without any catalyst (Table 2).

Classical thermal oxidation studies require a great length of time and the reaction control is very difficult. However, microwave oxidation decreases the reaction time and increases selectivity [12,13,22–25,28,29]. Thus, microwave power is very easy and clean to use for organic and inorganic syntheses. When compared to previous results, in the current study, the new synthesized catalysts are not quite effective on the oxidation of cyclohexane. On the other hand, these complexes showed good selectivity. It has been shown that the Cu (II), Co (II), Ni (II), and Mn (II) complexes of the ligands possess a catalytic effect. Cy–OH and Cy=O selectivity of the Cu (II) catalyst using microwave power is considerable when compared with the classical oxidation of CyH in the literature [9,10,12,13,23–29,30]. Niasari et al. synthesized a novel host (zeolite-Y)/guest (binuclear transition metal complexes)

nanocomposite materials used for cyclohexane oxidation. They found the conversion (mmol%) of cyclohexane in range from 8.7 to 40.3 [31]. Silva et al. prepared some Schiff base metal complexes to investigate for cyclohexane oxidation to cyclohexanone and cyclohexanol. Hence, they used the Fe (III), Fe (II), VO (IV) and Cu (II) complexes and found significant cyclohexane conversion and selectivity toward Cy–OH and Cy=O (Yield, 46%) [32]. Shylesh et al. prepared organic-inorganic hybrid mesoporous silica materials containing chromium and various organo trialkoxysilanes (chloropropyl, vinyl, methyl) and used them for oxidation reaction of cyclohexane. Cyclohexane oxidation reactions over various chromium catalysts were conducted and found the conversion (mol%) of cyclohexane in range from 3.4 to 10.2 according to the catalytic activity results of the mesoporous chromium catalysts. However, they reported high selectivity toward Cy-OH and Cy=O (29 and 63 mol%) [33]. In this paper, the best selectivity of the desired products was obtained with a silica-supported Cu (II)

Table 2 Catalytic oxidation of cyclohexane (CyH) with  $H_2O_2$  under microwave irradiation.<sup>a</sup>

| s (mmol%) |
|-----------|
|           |
|           |
|           |
|           |
|           |
|           |

<sup>a</sup> 400 watt power were applied for 75 min. The reaction temperature and pressure were held at around 110 °C and 30 bar in closed DAP60 vessels.

<sup>b</sup> 2 mmol cyclohexane: 4 mmol hydrogene peroxide and 5 mL acetonitrile were used in experiment without catalyst.

<sup>c</sup> 0.02 mmol catalyst:2 mmol cyclohexane:4 mmol hydrogene peroxide (1:100:200) and 5 mL acetonitrile were used for each reaction.



Fig. 5. Influence of the complexes in cyclohexane oxidation under microwave power. 0.02 mmol complex:2 mmol cyclohexane:4 mmol hydrogen 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.

complex, whereas the mmol percentages of the Cy–OH and Cy=O products are not quite as good (Fig. 5). The Ni (II) complex has a 7.31% cyclohexane conversion; however, its selectivity is not good enough because other further oxidized products arise. The catalytic effects of the Co (II) and Mn (II) complexes are approximately the same as the catalytic effect of the Ni (II) complex.

The new ligand "L<sup>1</sup>" has N and O donor atoms. The N and O atoms can promote a proton shift [30]. This situation may affect the oxidation reaction. The key point in the conversion of cyclohexane to the oxidized products is the reduction of Cu (II)–L<sup>1</sup> to Cu (I)–L<sup>1</sup>. This reduction to Cu (I)–L<sup>1</sup> is facilitated by the ligands that are available around the metal cations. The formation of the oxidation products, Cy–OH and Cy=O, show the preferential attack of the activated bonds. The high flexibility of Cu (I) complexes showing different geometries allows four-coordinated structures such as tetrahedral or trigonal-monopyramidal. Cu (II) complexes generally have square-planar or square-pyramidal geometries [34–36]. The tetrahedral flexibility of copper (I) compound facilitating the reduction to Cu (I) of the square-planar Cu (II) complex may be the reason why it has a higher selectivity than the other complexes.

### 4. Conclusion

In recent work, modified silica-supported azo-containing Schiff base and its Cu (II), Co (II), Ni (II) and Mn (II) complexes were synthesized, and then their structural determinations were carried out using NMR (<sup>1</sup>H and <sup>13</sup>C), FT-MIR/FIR, elemental analysis, ICP-OES,

TGA and a scanning electron microscope (SEM). The characterisation data confirmed the possible structure of the ligand and the complexes. To proceed, a clean and green oxidation of cyclohexane to cyclohexanol and cyclohexanone under microwave irradiation using H<sub>2</sub>O<sub>2</sub> as the oxidant was investigated by virtue of this novel solid phase-supported ligand containing an azo-group and its four transition metal complexes. As a result, it was found that the Cu-complex had selectivity towards the oxidation of cyclohexane to cyclohexanol and cyclohexanone with quite effective yields (6.73% and 4.87%) and with 42.99% conversion. In addition to showing fairly catalytic activity, these catalyst systems are easy to prepare. Moreover, in comparison to other systems they offer better advantages, such as the recovery, reusability and recyclability of the catalysts. Those characteristics were examined five times at the oxidation of cyclohexane and no significant changes were found in the catalytic activity. Finally, we believe that the most significant thing explained in this study is that it provides a new strategy for the design of novel azo-containing silica-supported catalysts.

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#### Appendix A. Supplementary material

Supplementary (Supplementary material data contain the NMR (<sup>1</sup>H and <sup>13</sup>C) spectra of the compound HMDB:L, Scanning electron microscopy images of the other complexes, TG of the silica-supported ligand (L<sup>1</sup>) and its complexes, FT-IR spectra of L and L<sup>1</sup>, and Thermogravimetric data of the ligand and the complexes.) data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.05.024.

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