

Synthesis and Metal Ion Uptake Studies of Silica Gel-Immobilized Schiff Base Derivatives and Catalytic Behaviors of their Cu(II) Complexes

Timur, Mahir

Altınözü Vocational School, Mustafa Kemal University, Hatay, TURKEY

Demetgül, Cahit⁺*

Department of Chemistry, Faculty of Arts and Sciences, Mustafa Kemal University, Hatay, TURKEY

ABSTRACT: *New silica supported Schiff base ligands were prepared by the condensation reaction of 4,6-diacetylresorcinol with silica-gel derivatives, which modified with 3-aminopropyltriethoxysilane and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. Metal ion uptake capacities of these compounds were studied towards of selected transition metal (Cd(II), Cu(II), Co(II), Mn(II), Pb(II) and Ni(II)) cations in an aqueous medium. In addition, Cu(II) complexes of these ligands were prepared by using heterogeneous reaction conditions. The synthesized compounds were characterized by using elemental analysis, FT-IR, DR-UV-vis., CP/MAS ¹³C-NMR, AAS, XRD and TGA techniques. Moreover, the morphological and chemical properties of these compounds were investigated by using a scanning electron microscope (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX). The catalytic performances of the Cu(II) complexes were investigated on H₂O₂ decomposition. These complexes displayed good catalytic activities towards the decomposition of H₂O₂ as heterogeneous catalysts.*

KEYWORDS: *Schiff Base; Metal-ion uptake; Heterogeneous catalysts; 4,6-diacetylresorcinol (DAR); Silica gel.*

INTRODUCTION

Silica gel is an amorphous inorganic polymer which composed of internal siloxane groups with silanol groups distributed on its surface [1-2]. The active hydrogen atoms of the silanol groups were dispersed on a silica gel surface which has the ability of reacting with trialkoxysilyl groups (e.g. 3-aminopropyltriethoxysilane) to give some organic nature to the inorganic support materials [3-4]. These organic groups, covalently bonded on the surface of

the inorganic support, are highly stable and resistant to removal from the surface by physical purification. Organofunctionalized silica gels are used extensively in many scientific and technological applications such as the stationary phase of chromatography, supports for microorganisms and pesticides [5], supports for catalysts in specific organic reactions and the extractions of metallic cations from aqueous and non-aqueous solvents [6-8].

* To whom correspondence should be addressed.

+ E-mail: cdemetgul@hotmail.com

1021-9986/2017/4/111-122

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The contamination of water sources by heavy metal pollutants is an important environmental concern. It is well known that heavy metal ions are non-biodegradable, toxic and tend to be stored in the human vital organs. Therefore, the removal processes of heavy metal ions from natural waters contaminated by these ions are attractive for environment [9]. A series of approaches can be applied to remove metal ions from the waters, by using the method of precipitation, exchanging, filtration and adsorption [10-11]. Among a series of important solid supports, silica gel shows a high thermal, chemical and mechanical stability [12] in metal ion pre-concentration [13]. Therefore, the main effect of the immobilization of Schiff bases on silica gel is to yield a new surface, which could be used as an adsorbent of heavy metal ion [14].

The complexes of Schiff bases containing N and O donor atoms which have been amongst the most widely studied coordination compounds are of particular interest [15] due to their structural lability, unusual configuration, sensitivity to molecular environments, ease of preparation and stabilization of both oxidation states of the metal usual in biological systems [16]. Currently, a number of Schiff-base copper complexes have been studied as enzyme mimics by their dioxygen binding ability, and catalytic activity in oxidative processes [17-18].

The decomposition of hydrogen peroxide has been used as a catalase model reaction for the investigation of the catalytic activity of various metals. The copper (II) complexes have been used as a catalase-like catalysts, but reports on this activity of copper (II)-containing systems reported are relatively limited [19]. The difference in reactivity of Cu(II) complexes towards H_2O_2 is due to the change in the redox potential of Cu(II) ions as a result of ligation with different ligands [20].

Homogeneous catalytic systems containing soluble metal complexes show excellent catalytic efficiencies under liquid phase condition [21-22]. But the separation of the homogeneous catalysts from the reaction medium at the end of the process is the main drawback of this type catalyst. In contrast, heterogeneous catalysts derived by immobilization of transition metal complexes on the solid support have gained considerable interest [23-24] due to the potential advantages like easy of separation, recovery, reusability, and the clean separation of product from the reaction mixture [25].

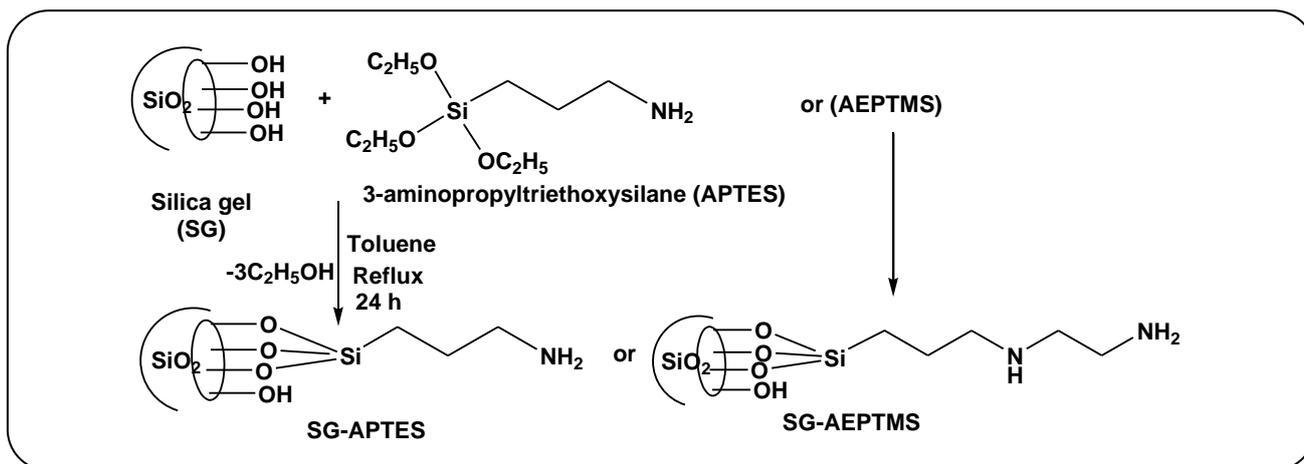
By these reasons; we aimed to synthesize new silica gel-immobilized Schiff base derivatives and their Cu(II) complexes. In addition, we investigated the metal ions uptake capacities of these Schiff base derivatives and the catalytic properties of Cu(II) complexes on hydrogen peroxide decomposition reaction.

EXPERIMENTAL SECTION

General

Silane coupling agents; 3-aminopropyltriethoxysilane (APTES) and N-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AEPTMS) were purchased from Aldrich. Silica gel (SG) 60 (0.015–0.040 mm) was purchased from Merck. 4,6-diacetylresorcinol (DAR) was prepared by following literature procedure [26]. Copper (II) ion was used as its acetate salt for Cu(II) complexes. Stock solutions of Cd(II), Cu(II), Co(II), Mn(II), Pb(II) and Ni(II) were prepared by dissolving the appropriate amount of metal(II) nitrate (analytical grade) in deionized water. The solutions of hydrogen peroxide were prepared freshly by dilution of 30% H_2O_2 (Merck) and were standardized daily by titration with a standard potassium permanganate solution. All other chemicals were analytically pure and used without any further purification.

Elemental analyses of the compounds for C, H and N were carried out with LECO-CHNS-932. The IR samples were prepared as KBr pellet. The investigation of IR properties of the synthesized compounds was carried out on a Perkin-Elmer RX-1 FT-IR spectrometer within the range of 4000–400 cm^{-1} . Room temperature diffuse reflectance spectra in the ultra- violet and visible region (DR-UV-vis) were recorded on a Varian Cary 100 model UV-Vis spectrophotometer. Solid-state ^{13}C -NMR spectra were obtained by using Cross-Polarization (CP) and Magic Angle Spinning (MAS), with Bruker 300 MHz Ultrashield spectrometer. Thermogravimetric analyses (TG-DTA) of the samples were performed with DuPont 951 thermal analyzer under air atmosphere, heated from 20 °C to 800 °C at a heating rate of 10 °C/min. Metal analysis was carried out by AAS Perkin-Elmer 3100 in a solution prepared by decomposition of the complex with HNO_3 followed by dilution with bidistilled water. X-Ray Diffraction spectrometry (XRD-powder) was obtained using a Rigaku System RadB X-Ray Diffractometer, using monochromated $CuK\alpha$ radiation in the range 2-40° (2 θ), at 25 °C. SEM/EDX analysis were performed on



Scheme 1: Immobilization of APTES or AEPTMS on silica gel surface.

an environmental SEM (JEOL JSM 55) coupled to energy dispersive X-ray spectroscopy EDX (OXFORD INSTRUMENTS INCA x-act). The samples were coated with a conductive layer of Au/Pd for SEM/EDX analysis.

Modification of silica gel

Firstly, silica gel (SG) was activated by refluxing with 6 M HCl for 12 h [27]. It was filtered, washed with deionized water until the filtrate was neutral and dried at 120 °C for 12 h. Silica gel was covalently modified by two silane coupling agents like 3-aminopropyltriethoxysilane (APTES) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEPTMS).

Silica gel (SG) + 3-aminopropyltriethoxysilane (APTES); (SG-APTES)

The activated white powder of silica gel (30 g) was suspended in 100 mL solution of 3-aminopropyltriethoxysilane prepared in dry toluene (10% v/v) [28]. The mixture was refluxed with stirring for 24 h under nitrogen atmosphere. The slurry was filtered and the resulting solid, SG-APTES was washed successively with excess amount of toluene, ethanol and diethyl ether, and then dried in the vacuum oven for 10 h (Scheme 1).

SG-APTES; White color powder, elemental analysis: C: 5.33; H: 1.76; N: 1.72%.

Silica gel (SG) + N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEPTMS); (SG-AEPTMS)

Activated silica gel (30.0 g) was suspended in 50 mL dry toluene. 10 mL of AEPTMS was added drop wise

to the suspension. Then, the mixture was refluxed with stirring for 24 h. The slurry was filtered and the resulting solid, SG-AEPTMS was washed with excess amount of toluene, ethanol and diethyl ether. The solid was dried in the vacuum oven for 10 h (Scheme 1).

SG-AEPTMS; White-gray color powder; elemental analysis: C: 8.57; H: 2.31; N: 3.42%.

Schiff base of SG-APTES; (SG-SB1)

0.65 g of 4,6-diacetylresorcinol (DAR) was dissolved in methanol (50 mL) and then added dropwise to the suspension of 5.0 g modified silica gel (SG-APTES) in methanol with magnetic stirring [29]. The mixture was refluxed for 24 h and a yellow-colored solid phase was filtered, washed with toluene-methanol (1:1) and dried under vacuum for 24 h. It was named as SG-SB1 (Scheme 2).

SG-SB1; yellow color powder; elemental analysis: C: 11.81; H: 1.94; N: 1.58%.

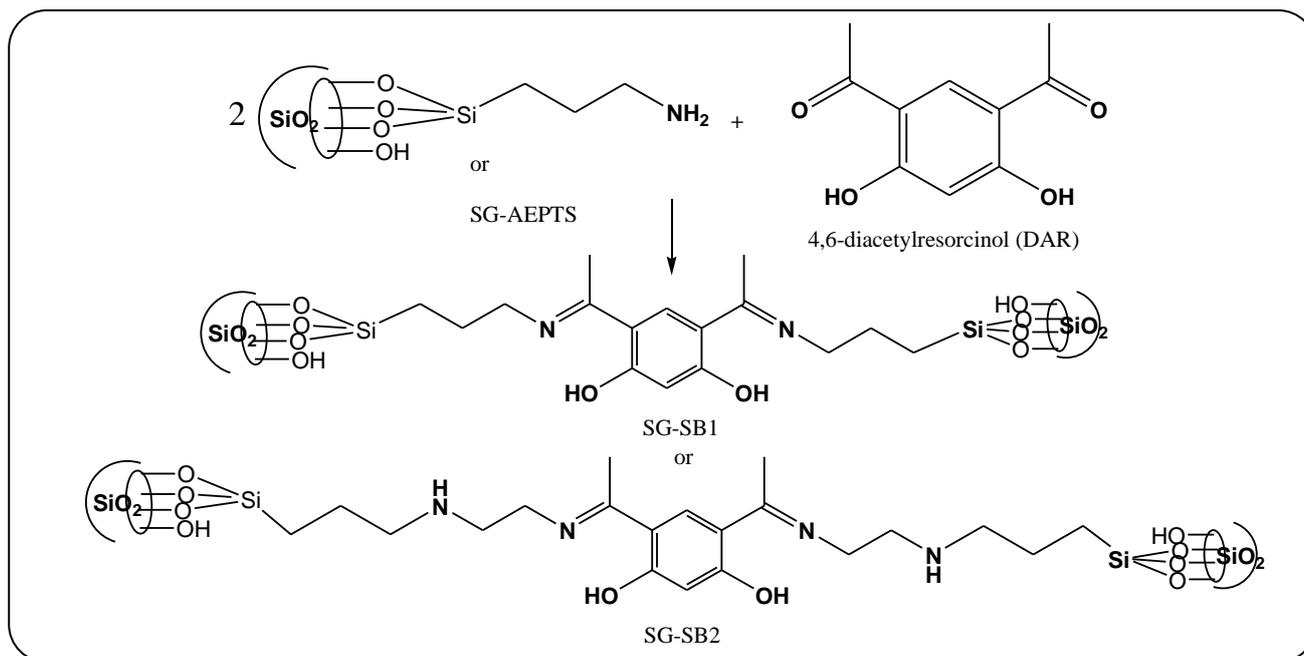
Schiff base of SG-AEPTMS (SG-SB2)

The other Schiff base was synthesized according to the same procedure of SG-SB1 by using 0.70 g of DAR and 5.0 g of SG-AEPTMS and named as SG-SB2 (Scheme 2).

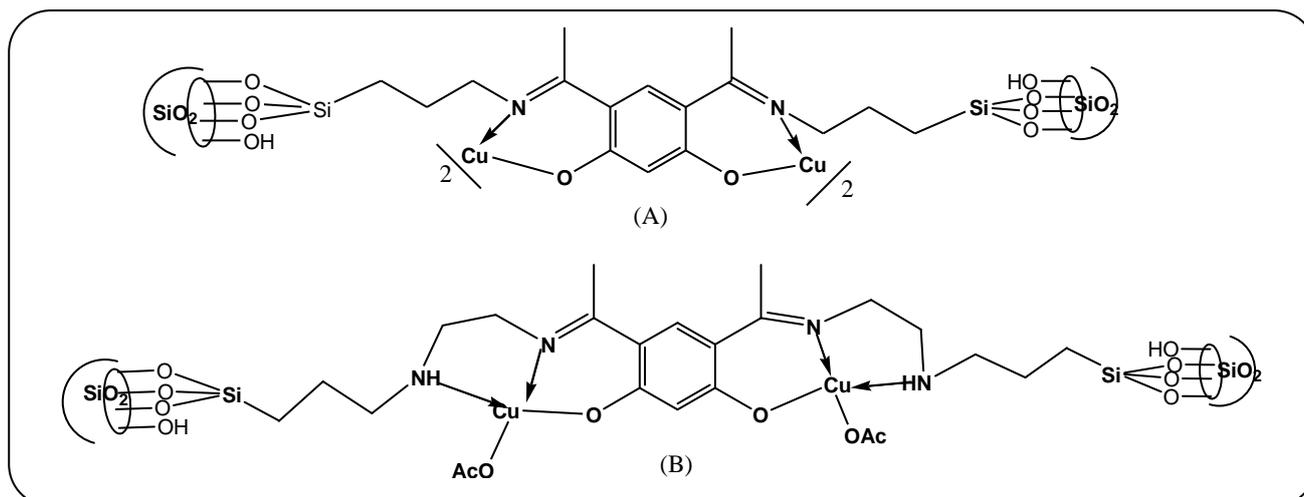
SG-SB2; yellow color powder; elemental analysis: C: 16.17; H: 2.93; N: 3.60%.

Synthesis of Cu(II) complexes

0.8g Cu(CH₃COO)₂.H₂O was dissolved in methanol and then added dropwise to the suspension of SG-SB1



Scheme 2: The proposed structure of silica supported Schiff bases (SG-SB1 or SG-SB2).



Scheme 3: The proposed structures of Cu(II) complexes of SG-SB1 and SG-SB2 (A: SG-SB1-Cu and B: SG-SB2-Cu).

(4.6 g) in methanol with magnetic stirring [30]. The mixture was stirred and refluxed for 24 h. After that the resulting green-colored compound was separated out, washed with methanol and dried under vacuum for 24 h. The complex was named as SG-SB1-Cu.

SG-SB1-Cu; Green color powder; elemental analysis (Cu %) 2.54%, 0.4 mmol/g⁻¹.

The other Schiff base-Cu(II) complex was synthesized according to the same procedure by using SG-SB2 and named as SG-SB2-Cu.

SG-SB2-Cu; Green color powder; elemental analysis (Cu %) 2.12%, 0.33 mmol/g.

The proposed structures of Cu(II) complexes are given in Scheme 3 (A and B).

Metal ion uptake studies

The metal ion uptake studies were performed by a batch technique in aqueous solutions for metal salts at 25 °C. A suspension of the SG-SB1 (or SG-SB2) powder on the metal ion solution of known volume and concentration

Table 1: Elemental (C,H,N) analysis results of the synthesized compounds.

Compound	C%	H%	N%	C/N
SG-APTES	5.33	1.76	1.72	3.10
SG-SB-1	11.81	1.94	1.58	7.48
SG-AEPTMS	8.57	2.31	3.42	2.51
SG-SB-2	16.17	2.93	3.60	4.49

was stirred for a definite time period over magnetic stirrer. The pH of the solution was adjusted using acetic acid/sodium acetate for pH 6.

The studies were performed using following procedure; 100 mL of aqueous solution of 100 mg/L metal ion buffered at pH 6 value was placed in contact with 0.10 g samples of SG-SB1 (or 0.15 g SG-SB2) for a period of 4 h by stirring. The conditions of this study were selected according to the literature includes similar studies [31]. After that, the suspension was filtered and the amounts of metal ions remaining in solution were determined by AAS. Likewise, the same procedures were followed for SG-APTES and SG-AEPTMS compounds in terms of comparability.

Catalytic activity studies

The decomposition of H_2O_2 catalyzed by Cu(II) complexes can be examined by titrating the undecomposed H_2O_2 with a standard $KMnO_4$ solution (0.01 M). The preferred concentration of H_2O_2 was 3.5×10^{-2} M. In addition, the chosen amount of catalyst was in the range from 0.01 mmol to 0.1 mmol Cu(II) at a constant concentration of H_2O_2 , pH and temperature.

The procedure for this study; 50 mg of SG-SB1-Cu complex (0.1 mmol Cu) was loaded in a flask containing a 10 mL of 3.5×10^{-2} M hydrogen peroxide solution in aqueous phosphate buffer pH 6.86. After that, the reaction flask was thermostatted to 25 °C under constant stirring. Finally, the extent of hydrogen peroxide decomposed at different intervals of time (each 10 min; from 0 to 60 min,) was estimated by taking 2.5 mL aliquots of the reaction mixture and titrating it with 0.01M $KMnO_4$ in the presence of 0.01 M H_2SO_4 . The process was duplicated at different amount of SG-SB1-Cu. The reusability of the catalyst was also examined. After each experiment, the solid was separated from the reaction mixture by simple filtration. Then, the catalyst was washed with water and dried carefully before using

in the subsequent run. The same experiments were performed for SG-SB1, SG-SB2 and SG-SB2-Cu.

RESULTS AND DISCUSSION

Solubility

The solubility experiments were done by using common solvents (i.e. water, ethanol, DMF, DMSO, THF). The results of these studies were shown that the synthesized compounds were insoluble in these solvents.

Elemental analyses

Results of carbon, hydrogen and nitrogen element analyses and the C/N ratio of SG-APTES, SG-AEPTMS, SG-SB1 and SG-SB2 are given in Table 1. The immobilization of APTES and AEPTMS onto the silica gel surface was confirmed by the determination of percentage values for C and N atoms in SG-APTES and SG-AEPTMS. On the basis of nitrogen elemental analysis, the amount of APTES and AEPTMS anchored onto silica was found in the range of 2.35-2.42 mmol/g. The results demonstrated that, carbon content was increased and nitrogen content was decreased after the condensation of DAR with SG-APTES and SG-AEPTMS because of the composition of DAR (not include nitrogen atom). Therefore, it can be easily seen the reason of the increase in the ratio of C/N for SG-SB1 and SG-SB2.

As a result of the AAS analyses, the %Cu(II) values of SG-SB1-Cu and SG-SB2-Cu, were found as 2.54% and 2.12% respectively.

DR-UV-vis spectra

The DR-UV-vis spectra of SG-APTES, SG-SB1 and SG-SB1-Cu are given in Fig. 1. There were important differences between the spectrum of SG-APTES and the spectrum of SG-SB1. On the spectrum of SG-APTES no peaks were observed in the range of 300-800 nm. In contrast, a new intense peak was observed at 381 nm in the spectrum of SG-SB1. The existence of this new peak

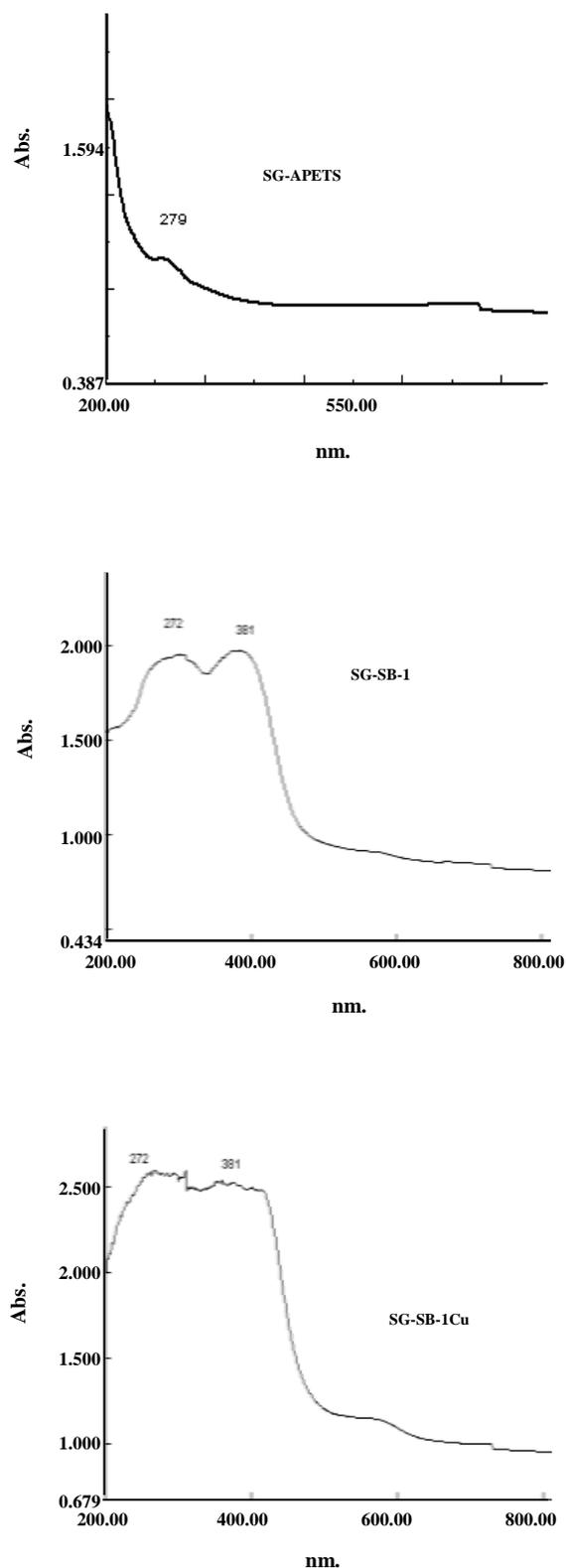


Fig. 1: DR-UV-vis spectra of SG-APTES, SG-SB1 and SG-SB1-Cu.

can be explained by the presence of the C=N groups (as π - π^* transition) of a Schiff base moiety. In addition, in the spectrum of SG-SB1-Cu, the peaks were broadened due to the chelation of Cu(II) ions with Schiff base. Also, a new peak was observed in low-intensity at 580 nm in the spectrum of SG-SB1-Cu attributed to the metal d-d transition [32]. On the other hand, similar spectra were obtained for the SG-AEPTMS, SG-SB2 and SG-SB2-Cu.

FT-IR spectra

It is well known in the literature that, the bands at 1086 and 803 cm^{-1} are assigned to the asymmetric and symmetric Si-O-Si stretching of silica gel, respectively. In addition, the bands at 967 cm^{-1} correspond to the silanol -OH groups. Likewise, the O-H stretching bands of silanol groups were observed in the range of 3430–3080 cm^{-1} .

In the spectra of SG-APTES and SG-AEPTMS, the characteristic bands of C-H and N-H stretching were observed in the region of 2800-3200 cm^{-1} [28].

The FT-IR spectra of SG-SB2 and SG-SB2-Cu are shown in Fig. 2. Unlike SG-AEPTMS, SG-SB2 had new bands in the range of 1300-1600 cm^{-1} . These new bands can be ascribed to the vibrational modes of C=N, C=C and C-H groups of the Schiff base moiety of the SG-SB2 [32]. In the spectrum of SG-SB2-Cu, the bands in that region were broadened and overlapped due to the chelation of Cu (II) ions with the Schiff base.

On the other hand, similar spectra were obtained for the SG-SB1 and SG-SB1-Cu.

CP/MAS ^{13}C -NMR

Further evidence supporting the formation of silica gel immobilized Schiff bases was provided by solid state ^{13}C -NMR spectra of SG-SB1, and SG-SB2 which are given in Fig. 3. On the other hand, the spectrum of SG-AEPTMS was given in “supplementary material” (Fig. S1). The ^{13}C -NMR spectral results of SG-APTES revealed that, no carbon signals were considered in the range of 60-200 ppm that is recognized from the literature by the similar studies [33]. The peaks seen in the range of 0-60 ppm attributed to the carbon atoms of -aminopropyl - part of SG-APTES [34]. In addition, new peaks were observed in the range of 100-120 ppm due to the aromatic ring carbons, 165-174 ppm attributed to phenolic carbons (C-OH) and 176-184 ppm assigned to the imine (C=N)

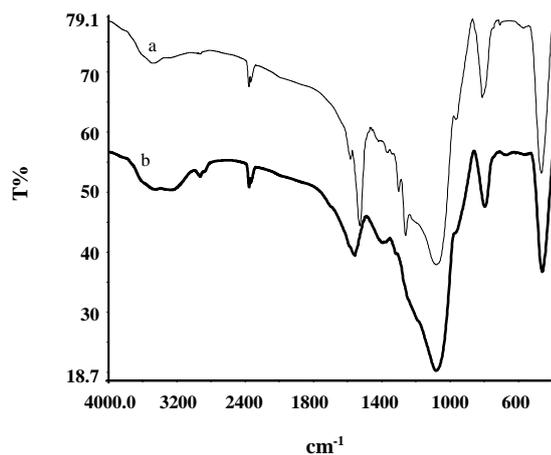


Fig. 2: The FT-IR spectra of SG-SB2(a), and SG-SB2-Cu(b).

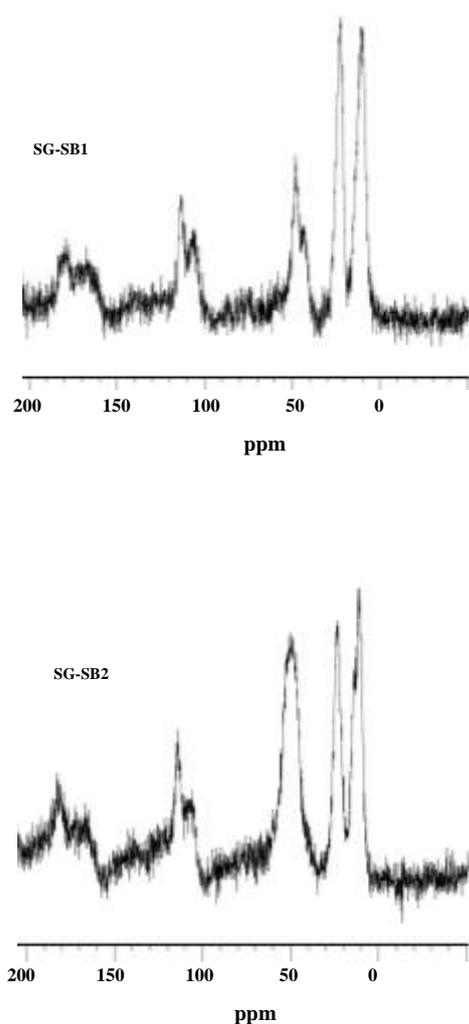


Fig. 3: CP/MAS ^{13}C NMR spectra of SG-SB1 and SG-SB2.

groups of Schiff base moiety of SG-SB1. The ^{13}C -NMR results of SG-SB1 were confirmed the condensation reaction between amine groups of SG-APTMS and carbonyl groups of the DAR. By the similar results; in the spectrum of SG-AEPTMS, carbon resonances of -N-(2-aminoethyl)-3-aminopropyl- chain were observed at 8, 22, 40, 50 and 55 ppm. On the other hand, in the spectrum of SG-SB2, the peaks at 50-55 ppm were overlapped because of the imine formation. Some new peaks were observed in the range of 165-175 ppm attributed to phenolic carbons (C-OH) and 177-184 ppm assigned to the imine (C=N) groups of Schiff base (SG-SB2) [30].

SEM/EDX

The morphology of SG-APTMS, SG-AEPTMS, SG-SB1-Cu and SG-SB2-Cu compounds was observed by SEM. Element distribution images of these compounds were obtained from EDX mapping. These SEM and EDX images are given in Fig. 4 and Fig. S2. The result of these analyses could be clearly shown that there were important changes occurred before and after immobilization of Schiff base Cu(II) complexes onto the SG-APTMS and SG-AEPTMS. In addition, the EDX mapping of these compounds confirmed the uniform distribution of the elements on the surfaces. Furthermore, the presence of copper in SG-SB1-Cu and SG-SB2-Cu materials could be clearly seen from these images while it was absent in SG-APTMS and SG-AEPTMS compounds.

XRD powder

The XRD patterns of SG-SB1, and SG-SB1-Cu are given in Fig. 5, and Fig. 6, respectively. In addition the X-Ray diffractograms of SG-SB2, and SG-SB2-Cu are given in Fig. S3-S4. It was reported that silica gel and APTES derivatives showed broad peaks in the range of $10\text{-}30^\circ$ 2θ because of the amorphous structure. Unlike Schiff base derivatives, the Cu(II) complexes had sharp peaks at $8\text{-}9^\circ$ might be assigned to coordination moiety.

TGA analysis

The thermal properties of the synthesized silica gel supported Schiff bases and their Cu(II) metal complexes were investigated by TG-DTG-DTA techniques. The TG-DTG-DTA curves of SG-SB1, SG-SB2, SG-SB1-Cu and SG-SB2-Cu are given in Fig. 7, Fig. S5-S7, respectively.

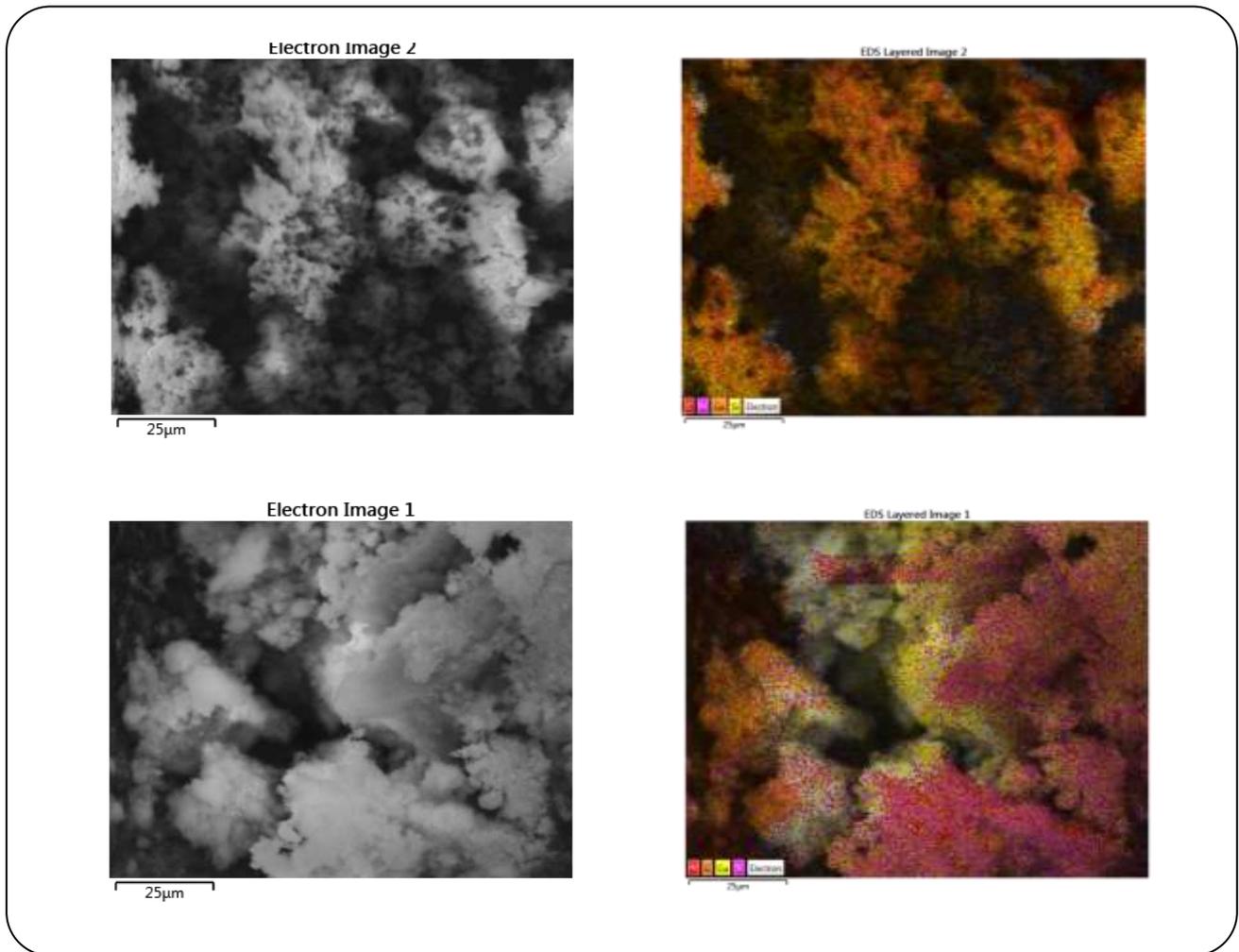


Fig. 4: SEM images of SG-SB1-Cu(a) and SG-SB2-Cu(b) and EDX images of SG-SB1-Cu(c) and SG-SB2-Cu(d).

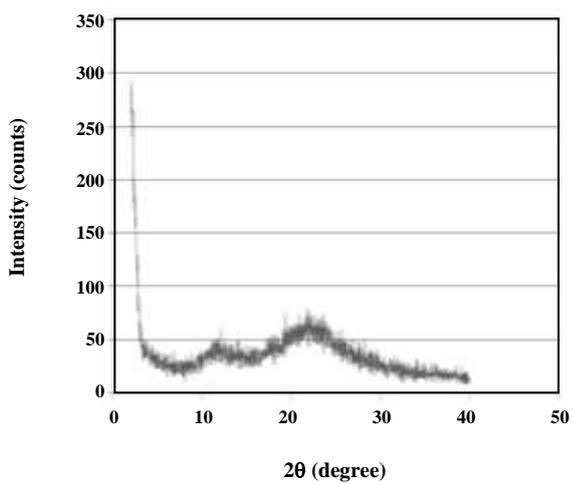


Fig. 5: The X-Ray diffractogram (XRD-powder) of SG-SB1.

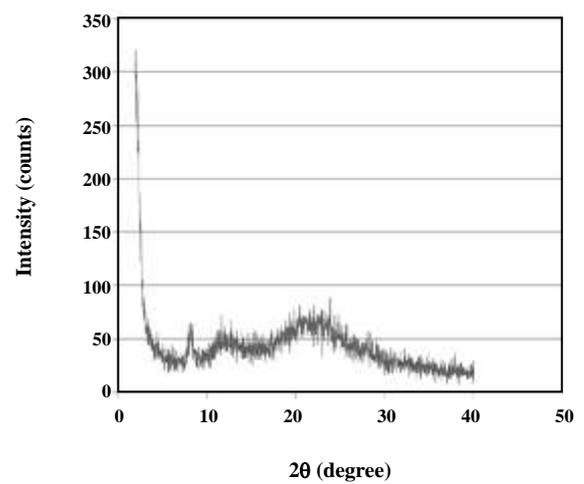


Fig. 6: The X-Ray diffractogram (XRD-powder) of SG-SB1-Cu.

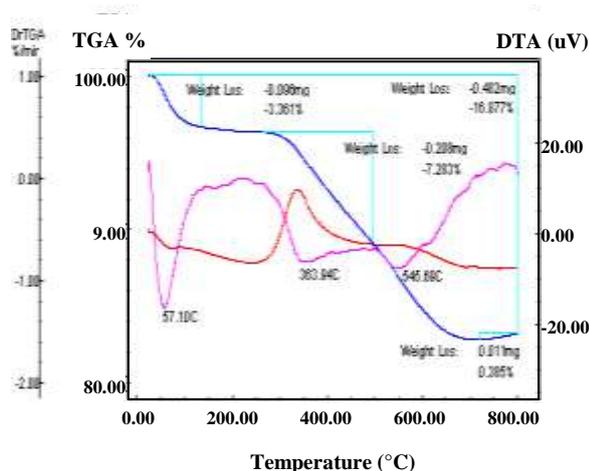


Fig. 7: The TG-DTG-DTA thermogram of SG-SB1.

It is well known that silica gel is a good adsorbent for moisture. Therefore, in the thermograms of the prepared materials, a weight loss of about 4-5% was observed in the range of 50-150 °C due to the loss of water adsorbed on the surface. In addition to the loss of adsorbed water, SG-APTES and SG-AEPTMS also displayed other significant weight losses (7-8%) in the region 200-600 °C, attributable to the loss of organic moieties immobilized on silica gel [35]. As a result of the analyses it can be easily stated that all of the compounds had thermal resistance up to the range of 250-300 °C. On the thermogram of Cu(II) complex, an increase in the weight of the compound was observed above 500 °C might be due to copper oxide formation.

Heavy metal ion uptake results

The results of metal ion uptake studies were given in mmol/g for metal ion bound to the surface of Schiff base supported silica gel (SG-SB1 and SG-SB2). And also, SG, SG-APTES and SG-AEPTMS were tested for the same ions to get a comparison. SG-SB1 and SG-SB2 exhibited a higher uptake capacity for Cu(II) ion (1.30-1.50 mmol/g) than the other metal ions used in this study. The metal ion uptake capacities for the other metal ions were found as Ni(II) (0.85-0.95 mmol/g), Fe(II) (0.60-0.64 mmol/g), Cd(II) (0.70-0.76 mmol/g), Co(II) (0.72-0.85 mmol/g), Mn(II) (0.65-0.72 mmol/g) and Pb(II) (0.53-0.60 mmol/g). The obtained data showed that the order of the overall uptake capacity of the Schiff base derivatives of Silica gel was Cu(II) > Ni(II) > Co(II) >

Cd(II) > Mn(II) > Fe(II) > Pb(II). Therefore, these studies were shown the SG-SB1 and the SG-SB2 displayed selectivity toward Cu (II) ions. The results of this study revealed that the metal uptake capacities of SG-SB1 and SG-SB2 were higher than the other compounds (SG, SG-APTES and SG-AEPTMS) due to the multidentate ligand character of the Schiff base moieties. The order of metal-ion uptake capacity of the prepared compounds was obtained as SG-SB2 > SG-SB1 > SG-AEPTMS > SG-APTES > SG due to the o-hydroxy Schiff base formation and additional secondary amine group of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEPTMS). Both of SG-APTES and SG-AEPTMS had a primary amine group increased the uptake capacity of neat silica gel surface by coordinating to the metal ions.

Catalytic activity results

The Schiff base-Cu(II) complexes immobilized on the silica gel surface were investigated as heterogeneous catalysts into the catalytic decomposition reaction of H₂O₂. The plots of hydrogen peroxide decomposition over SG-SB1, SG-SB2, SG-SB1-Cu, and SG-SB2-Cu as a function of reaction time are given in Fig. 8. It was noted that 60 minutes was an adequate response time for these catalytic reactions. The conditions of catalytic reactions for hydrogen peroxide decomposition were chosen as, 10 ml 3.5 × 10⁻² M H₂O₂, pH 6.86, time 60 min and temperature 25 °C, according to the similar studies in the literature [36]. Several of the amounts of SG-SB2-Cu were used to investigate the effects of the amount of catalyst on the catalytic performance. Thus, the plot of the experiment is given in Fig. S8.

Catalyst reusability

The reusability of immobilized catalyst is one of the most important benefits of heterogeneous catalysts. Therefore, heterogenization of homogeneous catalysts makes them useful for commercial applications. To investigate the stability and the reusability properties, the catalyst was separated from the reaction mixture after each experiment, washed thoroughly with dichloromethane and acetonitrile successively and dried before being used in the following experiment. The catalysts were successively reused five times without any loss of its catalytic activity. The filtrates were used for determination of the catalyst leaching by atomic

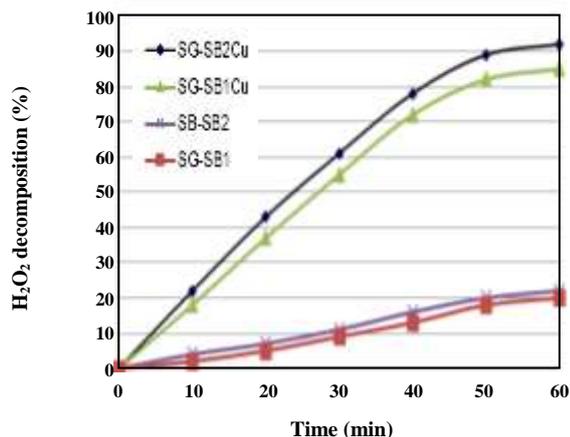


Fig. 8: H_2O_2 decomposition over the synthesized compounds as a function of reaction time.

absorption spectrometry (AAS). The results indicated that in the first run some catalyst was leached from organo-silica support (around 0.9%), but in the next runs no leaching was observed. After that, the catalyst was successively reused five times without any loss of its catalytic activity.

CONCLUSIONS

The characterization techniques used in this study were confirmed the structure of the silica supported Schiff base ligands. The order of the overall metal ion uptake capacities of the synthesized solid supported ligands were found as $Cu(II) > Ni(II) > Co(II) > Cd(II) > Mn(II) > Pb(II)$. The $Cu(II)$ complexes of SG-SB1 and SG-SB2 were investigated as heterogeneous catalysts on hydrogen peroxide decomposition reaction in aqueous medium. The prepared complexes showed good catalytic activity and reusability.

Supplementary Information

All additional information relating to characterization of the compounds using CP/MAS ^{13}C -NMR (Fig. S1), SEM-EDX (Fig. S2) X-Ray diffractograms (XRD-powder) (Figs. S3, S4), TG-DTG-DTA thermograms (Figs. S5, S6, S7), and the representation of influence of amount of SG-SB2-Cu on H_2O_2 decomposition (Fig. S8) are given in the supporting information.

Acknowledgment

The authors thank the Scientific and Technological Research Council (TÜBİTAK) for financial support (Project Number 111T023).

Received : Apr. 4, 2016 ; Accepted : Dec. 5, 2016

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