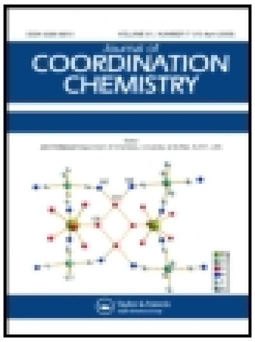


Taylor & Francis
Taylor & Francis Group

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Catalytic activity and electrochemical properties of Cu(II)-Schiff base complex encapsulated in the nanocavities of zeolite-Y for oxidation of olefins and sulfides

Saeed Rayati, Elham Khodaei & Majid Jafarian

To cite this article: Saeed Rayati, Elham Khodaei & Majid Jafarian (2017): Catalytic activity and electrochemical properties of Cu(II)-Schiff base complex encapsulated in the nanocavities of zeolite-Y for oxidation of olefins and sulfides, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2017.1369052

To link to this article: http://dx.doi.org/10.1080/00958972.2017.1369052

Publisher: Taylor & Francis
Journal: *Journal of Coordination Chemistry*
DOI: http://doi.org/10.1080/00958972.2017.1369052

Catalytic activity and electrochemical properties of Cu(II)-Schiff base complex encapsulated in the nanocavities of zeolite-Y for oxidation of olefins and sulfides

SAEED RAYATI*, ELHAM KHODAEI and MAJID JAFARIAN

Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran15418, Iran

Copper(II) complex of a Schiff base ligand (H_2L) was synthesized, characterizedand encapsulated in the cavities of zeolite-Y by a fixed ligand method. The zeolite encapsulated metal complex(CuL-Y)was characterized using FT-IR, UV-Vis and atomic absorption spectroscopy,thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), scanning electron microscopy images(SEM),energy-dispersive X-ray spectroscopy (EDX) and Brunauer-Emmett-Teller (BET). The catalytic activity and electrochemical behavior of the encapsulated complex has been studied in the oxidation of a wide range of sulfides and olefins using H_2O_2in ethanol. This heterogeneous catalytic system shows a dramatic increase in total turnover number (46,500) for oxidation of styrene. It could be readily reused for at least eightsuccessive times without discernible activity and selectivity deterioration, which displays potential for practical applications.

Keywords: Green oxidation; Heterogeneous catalyst; Zeolite-Y; Schiff base; Olefin; Sulfide

1. Introduction

Schiff base ligands and their metal complexes are attractive because of physicochemical properties of metal complexes and broad range of utilities in various areas of science such as electrochemical investigations, biological studies and catalytic fields [1-4]. Catalytic oxidation of organic compounds is an important domain of chemical research for producing valuable compounds. Although transition metal complexes are efficient homogeneous catalysts, one of the

---

*Corresponding author. Emails: rayati@kntu.ac.ir;srayati@yahoo.com major drawbacks of homogeneous catalysts is the problem of separation and recovery from the reaction mixture at the end of the process [5-7]. Nowadays, many researchers use different methods for catalyst recovery [8]. Indeed, using heterogeneous catalysts are capable of catalyzing organic reactions without obvious decrease in catalytic activity. Besides these methodologies, heterogenization of homogeneous catalyst via encapsulation or immobilization into solid support has been found to be advantageous over various other techniques which can provide high activity, selectivity and reusability of catalysts [9-12]. Several examples of heterogenization of homogeneous catalysts onto some inorganic supports, such as MCM-41 [13, 14], SBA-15 [15,16], nanomaterials and zeolites [17-19], have been explored. Among some of these supports, zeolites are excellent materials for encapsulation of transition metal complexes because of their low cost and intracrystalline cavities. In addition, the development of heterogeneous copper-based systems is another attractive area of research because of its unique characteristics, such as low toxicity, low price and powerful catalytic ability [20].In this study, in order to perform selective oxidation of sulfides to sulfoxides and olefins to the corresponding epoxy products, acopper(II) Schiff-base complex was encapsulated in thecavities of zeolite-Y.Furthermore, from green chemistry point of view, hydrogen peroxide is considered as the oxidant for oxidation reactions.

2. Experimental

2.1. *Instruments and reagents*

Infrared spectra were recorded as KBr pellets using UnicamMatson 1000 FT-IR. A Varian (AA 240) atomic absorption spectrometer was used for copper determination. X-ray powder diffraction (XRD) was carried out on a Philips PW 3710 diffractometer with CuKα radiation. Scanning electron microscopy (SEM) images were obtained on aVEGA3TESCANfield emission scanning electron microscope using HV voltage of 20 kV. The oxidation products were analyzed by HP Agilent 7890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm× 0.25 μm) and a flame ionization detector. Thermogravimetric analysis (TGA-DSC) was obtained using a Mettler-Toledo.Brunauer-Emmett-Teller (BET)micromeriticsTriStarII3020V1.03 is used as a high-quality surface area and porosity measurements by using the technique of gas adsorption.TheUV-Visabsorptionspectrawere measuredon Unico 4802 double-beam spectrophotometer. Electrochemical studies of catalysts were carried out by solartron model SI 1287 electrochemical interface. A glassy carbon (GC) disc electrode and graphite electrode were used as working and counter electrode, respectively.1,2-Propanediamine, 2,4-dihydroxyacetophenone,copper(II)nitratetrihydrate,hydrogen peroxide (solution 30% in water),tetrabutylammoniumhexafluorophosphate (TBAH)and zeolite-Y ($Na_{52}[(AlO_2)_{52}(SiO_2)_{140}]$)were obtained from Merck. Other materials were purchased from Sigma-Aldrich or Flukachemical companies.

2.2. *Preparation of bis(2,4-dihydroxyacetophenone)-1,2-propandiimine (H_2L)*

To a stirred ethanolic solution (20 mL) of 1,2-propanediamine(0.074 g, 1 mmol),2,4-dihydroxyacetophenone(0.304 g, 2 mmol) was added. The mixture was stirred and heated to reflux for 1 h. A yellow precipitate was filtered and washed with cold ethanol [21].$C_{19}H_{22}N_2O_4$: Yield (94%), m.p.= 180 °C. ^1H NMR (δ, in ppm): 1.26, 1.28 (d, 3H, $NCH_2CH(CH_3)N$), 2.2-2.49 (s, 6H, (CH_3)C=N), 3.3–3.7 (m, 1H, $NCH_2CH(CH_3)N)_2CH_2N$), 4.18-4.19 (m, 2H, $NCH_2CH(CH_3)N$), 6.01-7.41 (m, 6H, Ar*H*), 16.52–16.67 (s, 4H, OH). ^{13}C NMR (δ, in ppm): 14.34 ($NCH_2CH(CH_3)N$), 19.61 ($(CH_3)C=N$), 52.85 ($NCH_2CH(CH_3)N$), 54.06 ($NCH_2CH(CH_3)N$), 130–170 (Ar*C*), 172.36 ($(CH_3)C=N$).

2.3. *Preparation of copper(II) complex (CuL)*

The copper(II) complex was prepared as follows: the Schiff base ligand H_2L (0.34 g, 1 mmol) was dissolved in 20 mL ethanol. An ethanolic solution of copper(II) nitrate (0.31 g, 1.2 mmol) was added and the reaction mixture was refluxed for 2 h. The solution was concentrated to dark brown powders. The products were washed with cold ethanol and dried at 80°C. ($CuC_{19}H_{20}N_2O_4$: Yield (83%), m.p. = 265 °C.Anal. Calc. for $CuC_{19}H_{20}N_2O_4$ (403.92): C, 56.49; H,4.99; N,6.93. Found: C, 56.63; H, 4.91; N, 6.86%.

2.4. *Preparation of the Cu-Y*

Cu-Y was prepared by ion-exchange method. Copper(II) nitrate (3.1 g, 12 mmol) dissolved in 100 mL deionizedwaterwas addedto a suspension of 1.25 g Na-Y in deionized water (100 mL). The mixture was stirredunder refluxfor 24 hand the obtained solid was filtered off and washed with distilled water, and finally dried in 150 °C.

2.5. *Preparation of the CuL-Y*

Encapsulation of metal complex was performed with the flexible ligand method. Cu-Y (0.7 g) and 1.25 g of H_2L were mixed in 50 mL of methanol, and the reaction mixture was refluxed for 17 h in an oil bath under stirring. The resulting material was separated by filtration and then extracted with methanol using a Soxhlet extractor for 72 h to remove unreacted ligands from the cavities of the zeolite as well as those located on the surface of the zeolite along with neat complex. The unreacted metal ions present in the zeolite were removed by stirring with aqueous 0.01M NaCl solution. The resulting solid was filtered and washed with distilled water until free from chloride ions. Finally, it was dried at 120 °C. Scheme 1 shows the structure of copper complex encapsulated in the cavities of zeolite-Y.

2.6. *General procedure for catalytic oxidation of sulfides with hydrogen peroxide*

In a typical procedure, to a mixture of methylphenylsulfide (0.104 mmol, 12.31 μL) and catalyst (0.0013 mmol, 0.009 g) in ethanol (1 mL), H_2O_2 (1.04mmol, 81 μL) was added. The reaction mixture was stirred for 20 min at room temperature. The progress of the reaction was monitored by GC.

2.7. *General procedure for catalytic oxidation of olefins with hydrogen peroxide*

In a typical procedure, to a mixture of cyclooctene (0.072 mmol, 9.4 μL) and catalyst (0.0013 mmol, 0.009 g) in ethanol (1 mL), H_2O_2 (0.786 mmol, 50.80 μL) was added. The reaction mixture was heated to 50 °C for 1 h. The progress of the reaction was monitored by GC.

3. Results and discussion

3.1. *Characterization of the catalyst*

The FT-IR spectra of the Schiff base ligand, free complex, zeolite Na-Y and encapsulated complex are presented in table 1. The IR spectrum of the ligandexhibits a sharp band at 1630 cm^{-1}which is characteristic of azomethine group. Copper Schiff base complex showsa sharp band at1605cm^{-1} for C=N group. This indicates that the ligand is coordinated to the copper ion through the nitrogen atom of theazomethine group [22].The IR bands of the encapsulated complex are weak in comparison with the neat complex due to the low concentrations of metal complex in zeolite cages. The characteristic IR bands of the zeolite framework occur in the range 200-1300 cm^{-1}. The strong and broad band at 1000 cm^{-1} can be attributed to the asymmetric stretching vibrations of $(Si/Al)O_4$ units [23]. A broad band in the range 3200-3600 cm^{-1} is attributed to the surface hydroxyl groups [24].

Electronic spectral data of the ligand and complex in ethanol solution are summarized in table 2. The Schiff base ligand shows two intense bands which are assigned to$\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$transitions. Both bands are shifted to higher wavelengths in the complex, indicating coordination of the imine nitrogen atoms to the copper center. Ligand-to-metal charge transfer (LMCT) band was also observed at 344 nm for CuL. The free Cu-complex also showsa weak and broad band at 580 nm (CuL) which is assigned to d→dtransition. The electronic spectra of the encapsulated complex suggest the existence of Cu(II) Schiff base complex in the cage of zeolite, even though the peaks exhibit some shift and broadening compared to Cu-Y. This might be due to some distortions of the Cu(II) Schiff base complex occurring inside the zeolite cage.

The scanning electron micrographs for Na-Y andCuL-Y are shown in figure1. Analysis of the micrographs of Na-Y and the heterogeneous catalyst shows that there are no changes in the zeolite morphology or structure upon encapsulation.

The results of BET for Cu-Y andCuL-Y are shown in figure2. The surface area and pore volume of copper exchanged zeolite and the encapsulated copper complex are presented in table 3.The surface area of Cu-Y was 427.96 m^2g^{-1}.However, in the case of CuL-Y, the surface area was drastically reduced to 418.3 m^2g^{-1}. The average pore size of Cu-Y was 102.17 Å, and it reduced to 88.26 Å on CuL-Y [25]. The decrease in the pore volume clearly suggests that the metal complexwas encapsulated in the zeolite cavities.

The energy-dispersive X-rayspectroscopy (EDX) spectrumof Na-Y andCuL-Y (figure 3) showed the presence of N, O and Si as well as Cu in the encapsulated complex.The powder X-ray diffractograms of Na-Y and encapsulated Cu-complex are shown in figure 4.Comparison of the XRD pattern of zeolite Na-Y and the encapsulated Cu complex indicated no new crystalline pattern for the lattice. Therefore, the crystallinity of Cu-Y is almost intact after encapsulation of the complex [26]. These results further suggest that the reduction in surface area of the encapsulated complex is not due to any collapse of the crystalline structure [27].

The thermal properties of the copper(II) Schiff-base complex encapsulated in zeolite-Ywereinvestigated by TGA analysis method. The encapsulated copper complex was heated from

100 °C to 700 °C at a rate of 10 $°min^{-1}$ in nitrogen atmosphere. The thermogramisgiven in figure5. The endothermic peak observed at below 200 °C in the TGA curve is due to desorption of physically adsorbed and occluded water. The exothermic peak between 268-500 °C is attributed to the combustion of copper complex encaged in the host [28].

The Cu-content of the encapsulated catalyst determined by atomic absorption spectroscopy revealed that the metal content of the catalyst is 0.45 mmol per gram of the catalyst.

3.2. *Catalytic activity of the prepared catalyst*

The catalytic activity of the heterogeneous catalyst was investigated in the oxidation of various sulfides and olefins with hydrogen peroxide as green oxidant in ethanol. We first examined the oxidation of methyl phenyl sulfide and cycloocteneas the representative substrates for the optimization of reaction conditions withCuL-Y. In this study, several parameters, such as reaction time, temperature, molar ratios of the oxidant and the concentration of the catalyst were investigated during the optimization of the reaction.

3.2.1. Oxidation of sulfides. The oxidation of methyl phenyl sulfide with hydrogen peroxide in ethanol which led to the formation of only 13% product in the absence of catalyst was used as a model reaction. Different amounts of oxidant (H_2O_2) have been studied in the oxidation of methyl phenyl sulfide (table 4, entries 1-6). It was observed that oxidation of methyl phenyl sulfide required 10mmol of H_2O_2 for completion at 25 °C.

The catalytic activity has been remarkableinfluenced by the nature of the solvent and,therefore, catalytic potential of the heterogeneous catalyst in differentsolvents (acetonitrile, ethanol, dichloromethane and chloroform) was studied (figure 6) andthe highestconversion(100%)was obtained in ethanol and,consequently, ethanol as green solvent was selected for the oxidation of sulfides. The oxidation of different substrates with hydrogen peroxide necessitates the departure of an “OH” group in the form of hydroxyl anion (OH-) or water (H_2O). The higher dielectric constant of ethanol and acetonitrile as well as their hydrogen-bond forming ability assist departure of the leaving group and accelerate the oxidation reaction [29,30].

The effect of the catalyst concentration (0.003 g, 0.006 g and 0.009 g)was studied. The results are presented in figure 7. In the absence of catalyst, only13% of methyl phenyl sulfoxide was obtained and by increasing the amount of the catalyst, the catalytic potential of CuL-Y was improved.

Comparison of the catalytic activity of homogeneous catalyst (CuL) with the encapsulated one in the optimum conditions indicates littlelower catalyticactivity of the unsupported catalyst (CuL, 97%) in the oxidation of methyl phenyl sulfide. The heterogeneous catalyst can be recovered quantitatively by simple filtration and reused several times without significant loss of activity. The catalyst could be reused at least eight times without appreciable loss of its catalytic performance (table 5).

The heterogeneous catalystwas used for oxidation of a wide range of sulfides (table 6). The performance of thecatalystwasexcellent for the oxidation of various sulfides to their corresponding sulfoxides.

3.2.2. Oxidation of olefins. Catalytic activity of the encapsulated catalyst for oxidation of olefins with H_2O_2has been studied. Oxidation of cyclooctenewith H_2O_2 in the presence of catalytic amounts of CuL-Y led to the formation of cyclooctene oxide as the sole product (table 7). Thedifferentconcentrations of hydrogen peroxide have been examined and the results indicatedthat the maximum conversion was obtained at 10:1H_2O_2:cyclooctene molar ratio (table 7, entries 1-6).To optimize the solvent, oxidation of cyclooctene was conducted in different solvents (chloroform, acetonitrile, dichloromethane and ethanol)and resultsshow that the highest conversion (100%) was achieved in ethanol (table7, entries 6-9). The effect of temperature (25, 35, 50 and 55°C) on the heterogeneous oxidation of cycloocteneshows that an increase in the reaction temperature to 55°C results ina decrease of reaction time to 1 h (table 7, entries 10-13). The effect of catalyst concentration (0.003 g, 0.006 g and 0.009 g) on the oxidation of cyclooctene shows that in the absence of catalyst,only 9% cyclooctene oxide was obtained while in the presence of 0.009 g CuL-Y,complete conversion of cyclooctene was achieved (table 7, entries 13-16).

Thelower catalytic activity of the homogeneous catalyst(CuL, 93%) with respect to the encapsulated ones in the oxidation of cyclooctene may be due to the degradation of the homogeneous catalyst. Also the oxidation of cyclooctene in the presence of Cu-Y proceeds very slowly and leads to the formation of only around 9% product.The solid catalyst could be easily recoveredfrom the reaction mixture by direct filtration and reused multiple times (table 8).

In orderto investigate the efficiency of the heterogeneous catalyst, further investigations were carried out ona wide range of olefins (table 9). Excellent conversion and selectivity forepoxide products were obtained within 1 h for a wide range of the olefins.

Many Schiff base complexes have been reported for olefin epoxidation. The results of the oxidation of cyclooctene in the presence of various heterogeneous complexes are summarized in table 10. Comparison of this catalytic system with previously reported systems shows that higher conversion and selectivity in the shorter reaction time was achieved in the oxidation of cyclooctene.

In order to estimate the longevity of the heterogeneous catalytic system, total turnover number (TON) has been studied. The catalyst exhibited excellent activities for oxidation of styrene in ethanol solution under mild conditions (Cat:Styrene:H_2O_2 is 1:50,000:600,000) with a TON of 46,500 for CuLafter 24 h which is one of the highest values reported for Schiff base complex encapsulated in zeolite-Y.

3.3. *Electrochemical studies*

The electrochemical behavior of the copper(II) complex as heterogeneous catalyst for the oxidation of methyl phenyl sulfide or cyclooctene in the potential range of -3 to +3 V in CH_3CN containing 0.1 M TBAH as the supporting electrolyte at scan rate of 100 mVs^{-1} has been studied (figure8).In this study, calomel (Hg/Hg_2Cl_2), graphite and glassy carbon were used as the reference electrode, counter electrodeand working electrode, respectively.Voltammetric study showed a higher current intensity for copper encapsulated complex compared to the blank experiments which illustratethe important role of the catalyst in oxidation of sulfides (figure8). Cyclic voltammograms of glassy carbon/CuL-Y in the presence of 80 mmolof methyl phenyl sulfide using 800 mmol H_2O_2 at various scan rates are displayed in figure9. The oxidation or reduction peaksbecame broader with increasing scan rate. In addition, at higher scan rates, the oxidation peaksshiftedto more positive potentials for sulfide oxidation which indicates that the electro-oxidation of copper species to higher valance state is much faster than the catalytic oxidation of substrates. This reveals thatan increasein scan rate decreasesthe rate of sulfideoxidation. Furthermore, the anodic peak currents that are linearly proportional to the square root of scan rate suggest that the overall oxidation of sulfide at this electrode is controlled by the diffusion of sulfide to the surface redox sites [33].Chronoamperograms of the acetonitrile solution of the CuL-Yand blank in the presence of methyl phenyl sulfide (figure10) or cyclooctene(figure 9) exhibited the higher catalytic activity of the catalyst compared to the blank one. This result was revealed from the current intensity in oxidation and reduction potentials. Similar results were achieved in the oxidation of cyclooctene in the presence ofheterogeneous catalyst. The growth of reduction and oxidation peaks for heterogeneous catalystcompared to the blank one illustrated the importance of the catalyst in the oxidation of olefins (figure9).

4. Conclusion

Atetradentate (N_2O_2) Schiff base ligand (H_2L) and its corresponding copper(II) complex (CuL) was synthesized and encapsulated in the cavities of the zeolite-Y. The heterogeneous catalyst was characterized by different techniques. Selective oxidation ofvarious sulfides to sulfoxides and olefins to epoxides is foundto enhance in the presence of the encapsulated complex using H_2O_2 as green oxidant in ethanol by approaching to the green chemistry. During reusability experiments, the heterogeneous catalyst was able to recovered and reusedinmultiple consecutiverunswithout loss in activity or selectivity. The synthesized heterogeneouscatalyst exhibited excellent activity foroxidation of styrene in ethanol with a turnover number of 46,500 (CuL-Y) after 72 h, which is one of the highestvalues reported for a heterogeneous catalytic system.In addition, the electrochemical behavior of CuL-Y was investigated in different conditions by cyclic voltammetry and chronoamperometrytechniques.

Acknowledgements

The financial support of this work by K.N. Toosi University of Technology research council is acknowledged.

References

[1] H.H. Gong, K. Baathulaa, J.S. Lv, G.X. Cai, C.H. Zhou. *Med. Chem. Commun.*,**7**, 924 (2016).

[2] M. Aghayee, M.A. Zolfigol, H. Keypour, M. Yarie, L. Mohammadi.*Appl. Organomet. Chem.*,**30**,612 (2016).

[3] W.G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, E.H. Sheng.*J. Organomet. Chem.*,**35**,503

(2016).

[4] S. Kato, M. Kanai, S. Matsunaga.*Chem- Asian J.*,**8**,1768 (2013).

[5] A. Dewaele, F. Verpoort, B. Sels.*ChemCatChem.*,**8**, 3010 (2016).

[6] M. Opanasenko, P. Stepnicka, J. Cejka.*RSC Adv.*,**4**,65137 (2014).

[7] M. Nikoorazm, A. Ghorbani-Choghamarani, M.Khanmoradi.*RSC Adv.*,**6**, 56549 (2016).

[8] S. Rezaei, A.G. Choghamarani, R. Badri.*Appl. Organomet. Chem.*, **30**,985 (2016).

[9] M. Kazemnejadi, A.R. Sardarian.*RSC Adv.*, **6**,91999(2016).

[10] H. Keypour, S.G.Saremi, H. Veisi, R. Azadbakht. *RSC Adv.*, **6**,77020(2016).

[11] K.J. Dunst, B. Scheibe, G. Nowaczyk, S. Jurga, P. Jasiński. *P. Meas. Sci. Technol.*, **28**, 1133 (2017).

[12] S.H. Dave, C. Gong, A.W. Robertson, J.H. Warner, J.C. Grossman.*ACS Nano.*, **10**, 7515(2016).

[13] N. Pal, A. Bhaumik.*RSC Adv.*, **5**, 24363(2015).

[14] M. Ferré, R. Pleixats, M.W. Man, X. Cattoën. *Green Chem.*, **18**,881 (2016).

[15] E. Lam, J.H.T. Luong.*ACS Catal.*, **4**,3393(2014).

[16] T. Krawczyk, K. Jasiak, A. Kokolus.*Catal.Lett.*,**146**, 1163(2016).

[17] X.Z. Shu, S.C. Nguyen, Y. He, F. Oba, Q. Zhang, C. Canlas, G.A. Somorjai, A.P. Alivisatos, F.D.Toste.*J.Am.Chem.Soc.*, **137**, 1163(2015).

[18] T. Ennaert, J.V. Aelst, J. Dijkmans, R.D. Clercq, W. Schutyser, M. Dusselier, D. Verboekend, B.F. Sels. *Chem. Soc. Rev.*, **45**, 24363(2016).

[19] S.C. Oh, T. Nguyendo, Y. He, A. Filie, Y. Wu, D.T. Tran, I.C. Lee, D. Liu.*Catal. Sci. Technol.*, **7**,24363 (2017).

[20] Y. Hou, N. Wang, J. Zhang, W. Qian.*RSC Adv.*, **7**,14309 (2017).

[21] S. Rayati, S. Shokoohi, E. Bohloulbandi.*J. Iran. Chem. Soc.*, **13**,14309 (2016).

[22] A.A. Adel, E. Azza, A.A. Abou-Hussein. *Spectrochim. Acta, Part A*, **64**,1010(2006).

[23] K.O. Xavier, J. Chacko, K.K.M. Yusuff.*Appl. Catal. A: Gen.*, **258**, 251(2004).

[24] A. Mobinikhaledi, M. Zendehdel, S.M.B. Hosseini-Ghazvini, P. Safari. *Transition Met. Chem.*, **40**, 313(2015).

[25] A. Mobinikhaledi, M. Zendehdel, P. Safari.*Reac. Kinet. Mech. Cat.*, **110**,497 (2013).

[26] A. Shoumkova, V. Stoyanova.*J. Porous Mater.*,**20**,249 (2013).

[27] G.R. Reddy, S. Balasubramanian.*Microporous Mesoporous Mater.*, **231**, 207(2016).

[28] M. Sharma, B. Das, G.V. Karunakar, L. Satyanarayana, K.K. Bania.*J. Phys. Chem. C*, **120**, 13563 (2016).

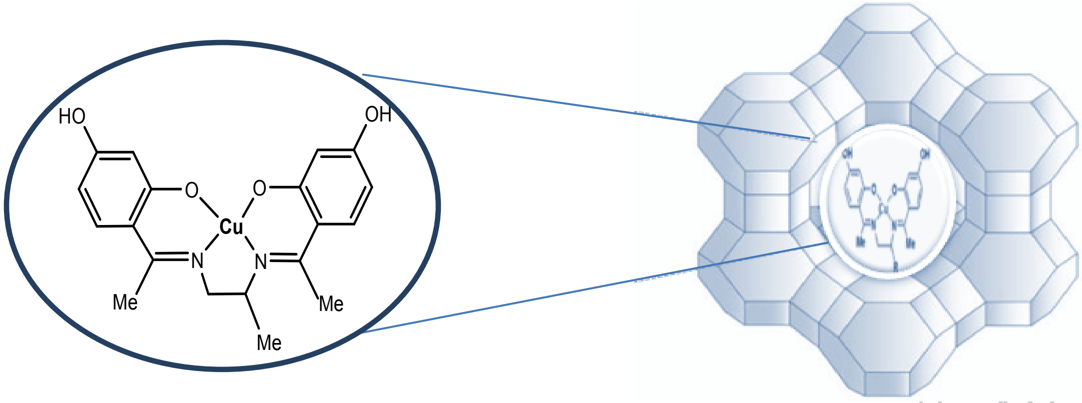
[29] S. Zakavi, A. Abasi, A.R. Pourali, S. Talebzadeh. *Bull. Korean Chem. Soc.*, **33**, 35 (2012).

[30] D. Mohajer, G.Karimipour, M.Bagherzadeh. *New J. Chem.*,**28**, 740 (2004).

[31] M. Bagherzadeh, M. Zare. *J.Coord.Chem.*,**65**, 4054 (2012).

[32] M. Lashanizadegan, E.Parvizi.*Met.-Org. Nano-Met.Chem.*, **45**, 1154 (2015).

[33] R.S. Nicholson, I. Shain. *Anal. Chem.*, **4**,36 (1964).



Scheme 1. Proposed framework structure of zeolite encapsulated metal Schiff base complexes.

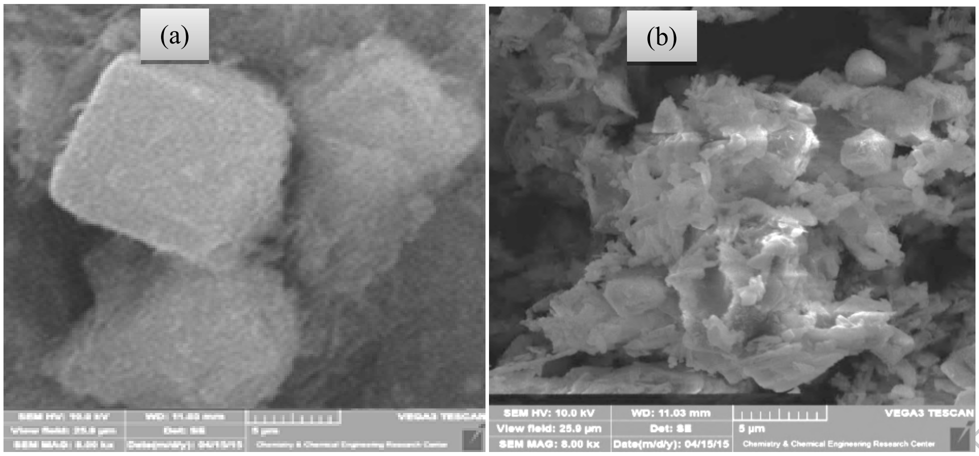


Figure 1. SEM photographs of (a) Na-Y (b) CuL-Y.

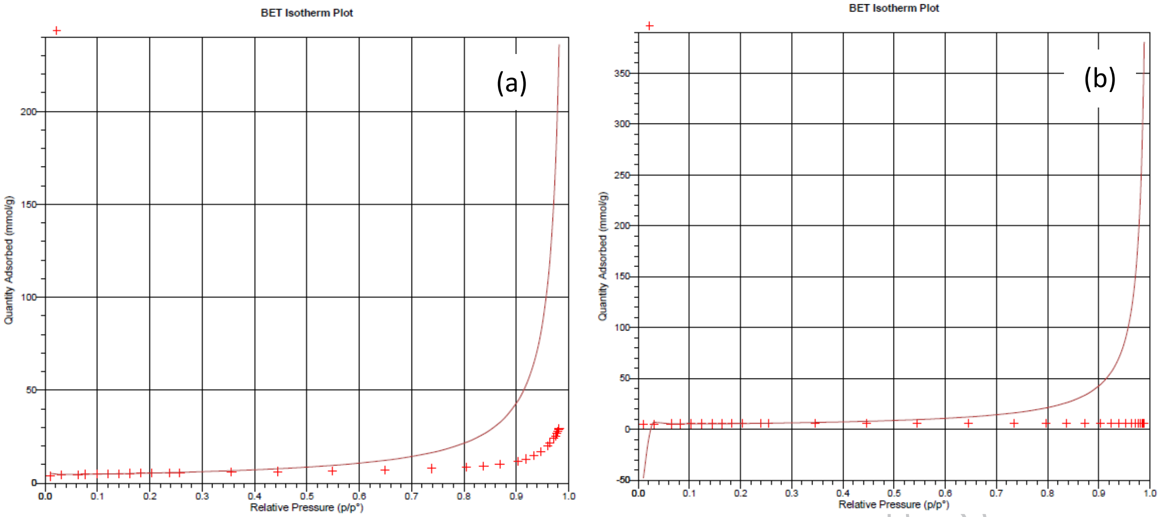


Figure2.N_2 isotherms of (a)Cu-Y and (b) CuL-Y with their pour volume.

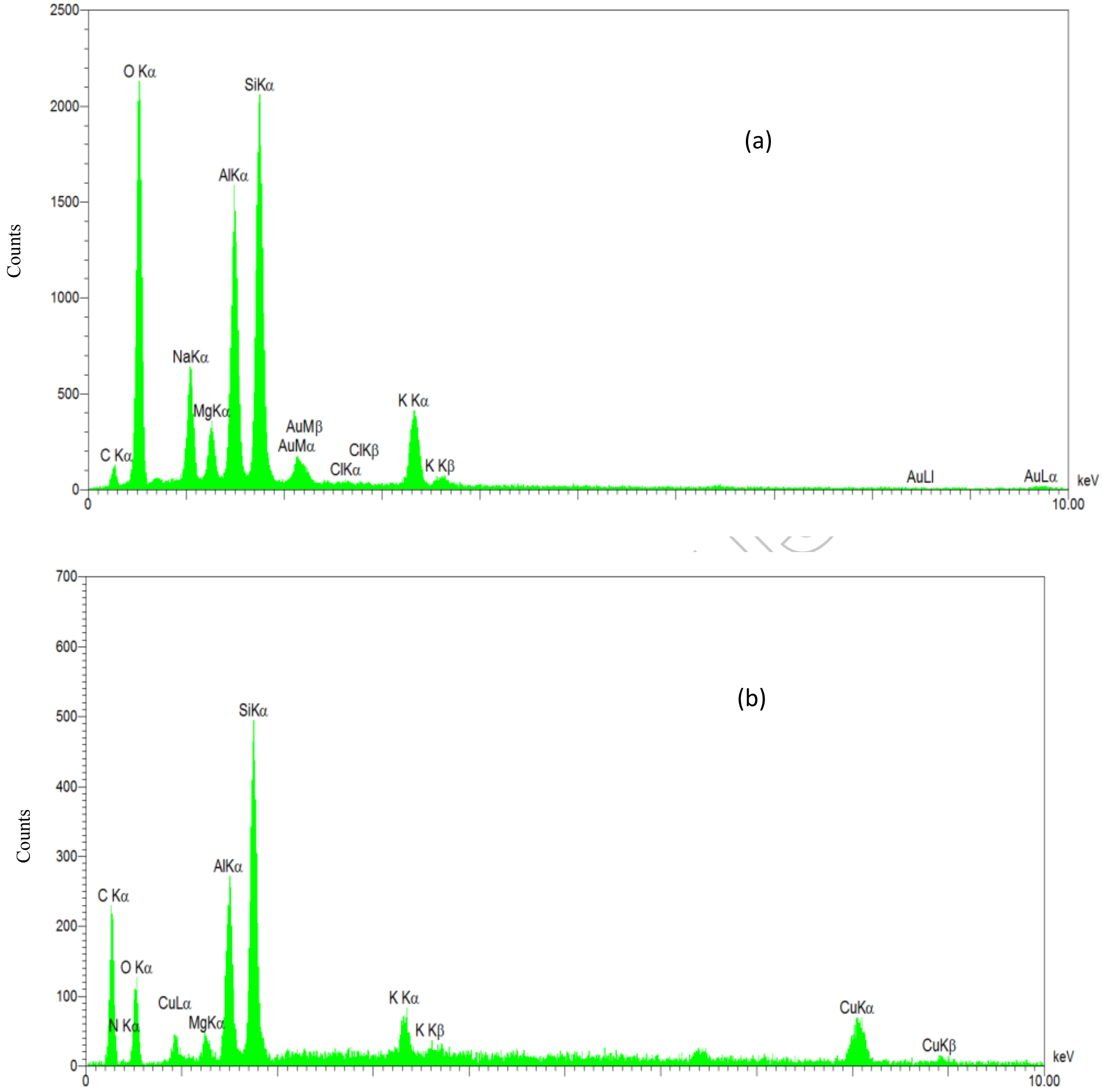


Figure3. The energy-dispersive X-ray spectroscopy (EDX) spectrum of (a)Na-Y and (b) CuL-Y.

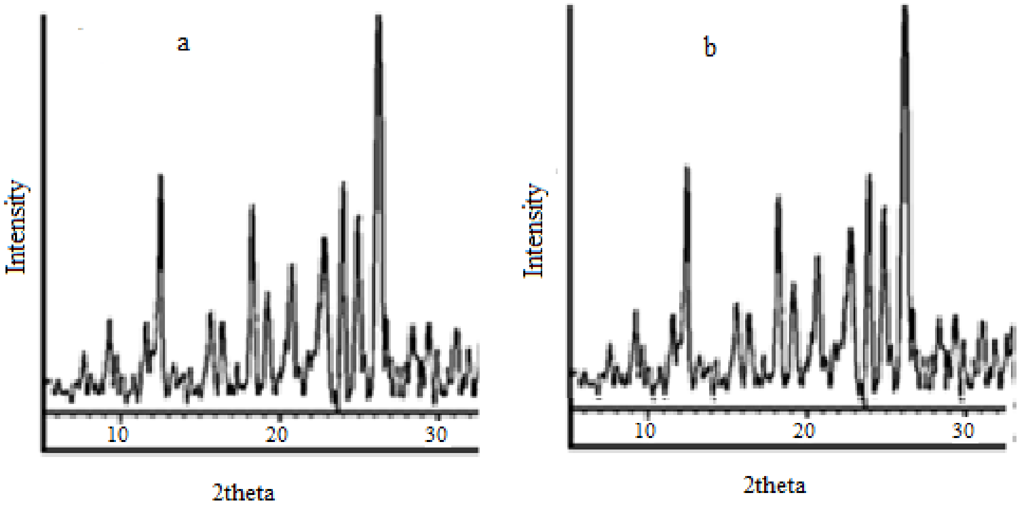


Figure4. XRD patterns of (a) Cu-Y and (b) Cu_1-Y.

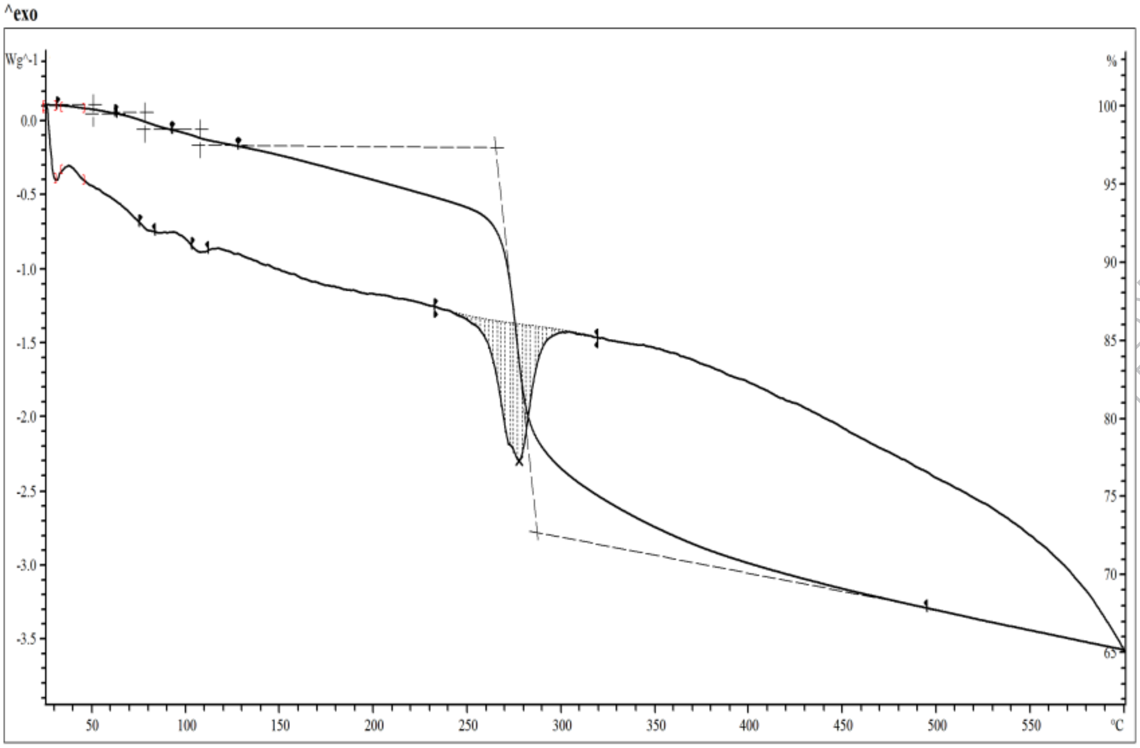


Figure5. (a) TGA curves of the CuL-Y.

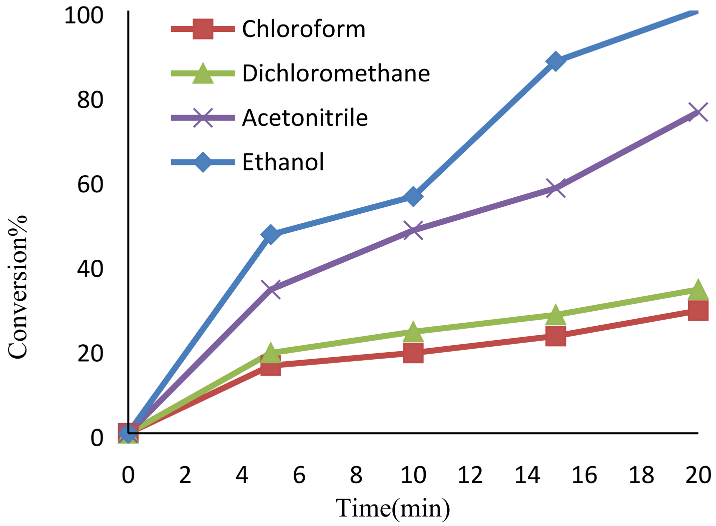


Figure 6. The effect of various solvents on the oxidation of methyl phenyl sulfide with H_2O_2in the presence ofCuL-Y.Reaction conditions: catalyst(mmol):sulfide:H_2O_2 is 1:80:800 at 25°C.

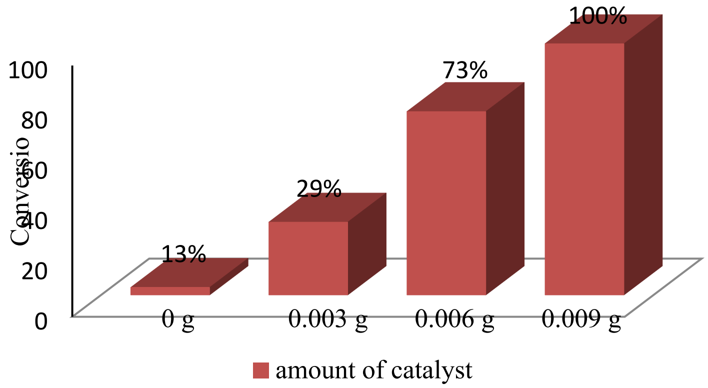


Figure 7. The influence of catalyst concentration on the oxidation of methyl phenyl sulfidewith H_2O_2 catalyzed by CuL-Y.

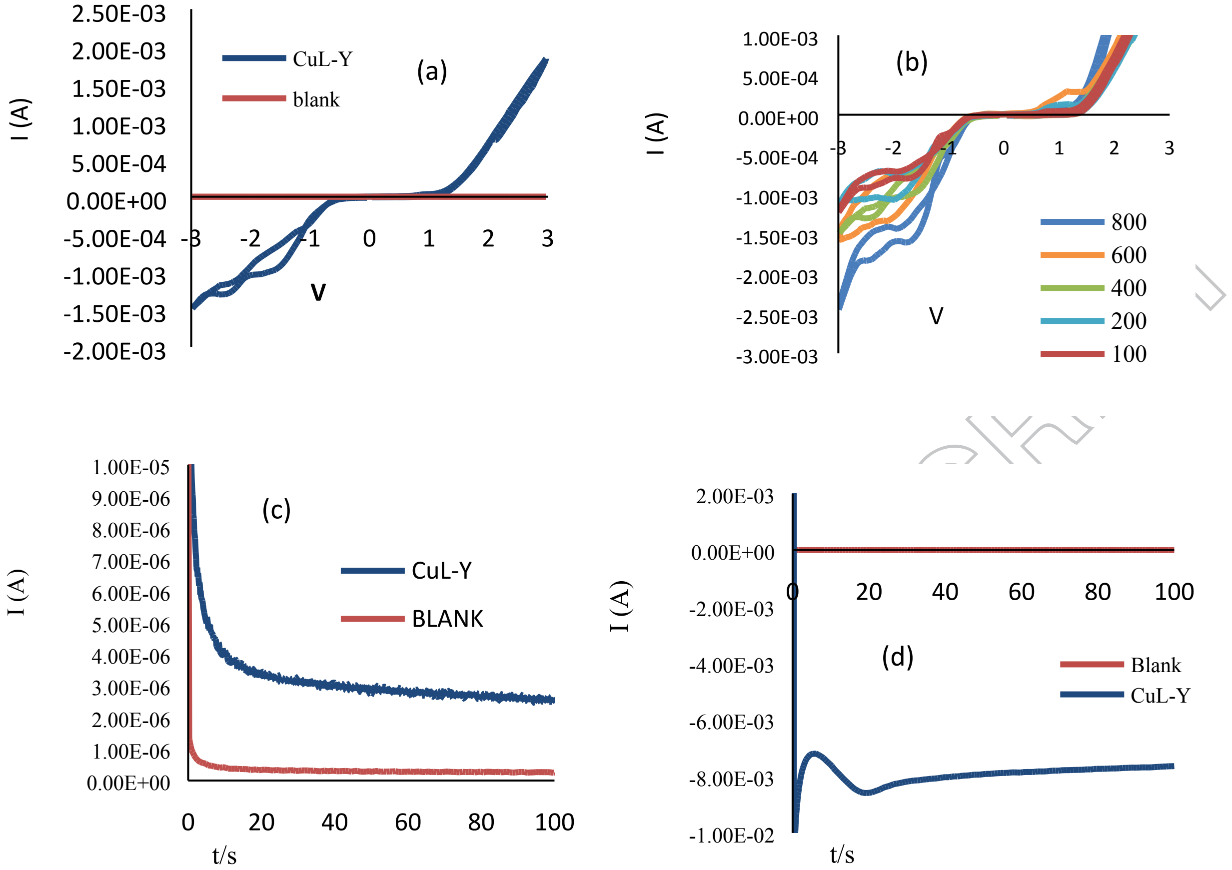


Figure8. The voltammetric behavior of (a) CuL-Yand blankat 100 mV/s.The voltammetric behavior of (b) CuL-Y at different scan rates (100, 200, 400, 600, 800 (mV/s)).Chronoamperograms of (c) CuL-Yand blankin oxidation potential (0.89 V) and (d) in reduction potential (-1.64 V) in EtOH for oxidation of methyl phenyl sulfide. Reaction conditions: catalyst(mmol):methyl phenyl sulfide:H_2O_2 is 1:80:800 at room temperature between -3 and +3 V in acetonitrile solution containing 0.1 M TBAH as supporting electrolyteand calomel (Hg/Hg_2Cl_2), graphite and glassy carbon were used as the reference electrode, counter electrodeand working electrode, respectively.

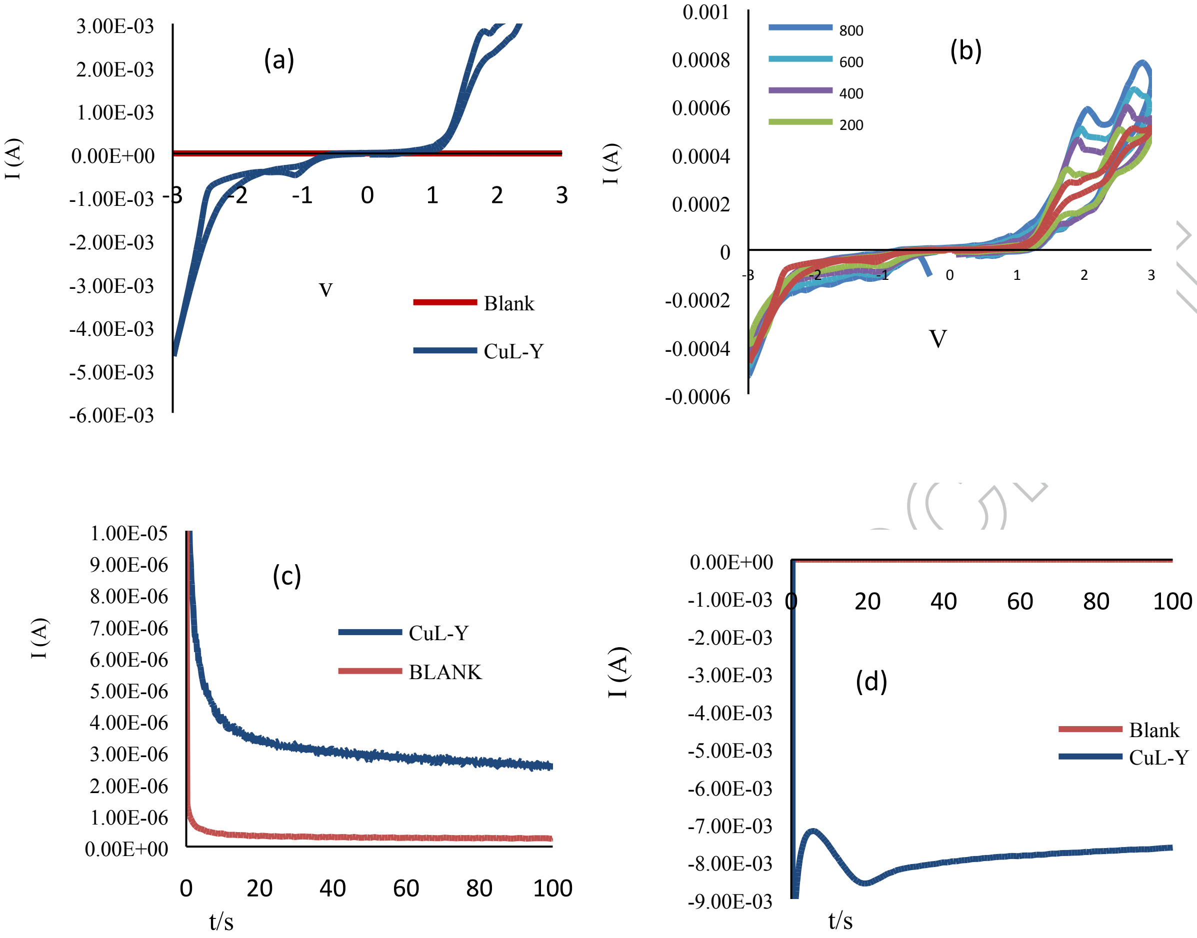


Figure9. The voltammetric behavior of (a) CuL-Yand blankat 100 mV/s.The voltammetric behavior of (b) CuL-Y at different scan rates (100, 200, 400, 600, 800 (mV/s)).Chronoamperograms of (c) CuL-Yand blankin oxidation potential and (d) in reduction potential in EtOH for oxidation of cyclooctene. Reaction conditions: catalyst(mmol):sulfide:H_2O_2 is 1:50:500at room temperature between -3 and +3 V in acetonitrile solution containing 0.1 M TBAH as supporting electrolyte and calomel (Hg/Hg_2Cl_2), graphite and glassy carbon were used as the reference electrode, counter electrodeand working electrode, respectively.

Table 1. IR spectral data (wavenumbers in cm^{-1}) of ligands and zeolite encapsulated metal complexes.

Samples	$\nu_{(\text{ Al-O-Si})}$	$\nu_{(\text{Al-O-Si})}$	$\nu_{(\text{C=C})}$	$\nu_{(\text{C=N})}$	$\nu_{(\text{O-H})}$
H_2L	-	-	1537	1630	3410
CuL	-	-	1534	1605	3474
Cu-Y	795	1021	-	-	3506
CuL-Y	794	1168	1536	1630	3512

Table 2. Electronic spectral data of the ligand and copper(II) complex encapsulated in zeolite in ethanol.

Compound	λ_{max} (nm)(ε, $M^{-1}cm^{-1}$)	Assignment
H_2L_1	227 (3373)	π→π*
	312 (2881)	n→π*
CuL	239 (21686)	π→π*
	298 (15420)	n→π*
	344 (9363)	MLCT
	580 (800)	d-d
CuL_{1}-Y	230	π→π*
	296	n→π*
	373	MLCT
	583	d-d

Table 3. Textural properties of Cu-Y and its complex-encapsulated analogue.

Sample	S_{BET} (m^2g^{-1})	Average pore size(Å)	Pore volume(cm^3g^{-1})
Cu-Y	427.9644	102.1748	1.093179
CuL-Y	418.3000	88.2604	0.922983

Table 4.The effect of amount oxidant and temperature on the oxidation of methyl phenyl sulfide in the presence of CuL-Y in ethanol.[a]

Entry	mmol sulfide/oxidant	Time (min)	Temperature (°C)	Conversion %
1	1:1	20	25	6
2	1:2	20	25	15
3	1:3	20	25	26
4	1:4	20	25	38
5	1:5	20	25	53
6	1:10	20	25	100

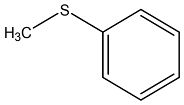
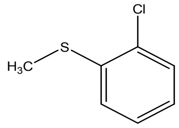
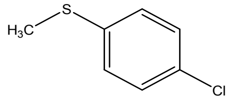
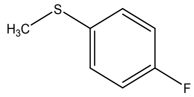
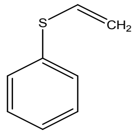
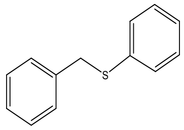
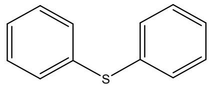
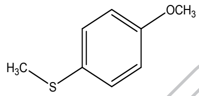
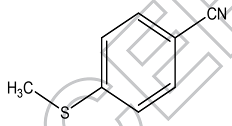
[a] Reaction conditions: catalyst(mmol):methyl phenyl sulfide is 1:80.

Table 5.Reuse of the heterogeneous catalysts in the oxidation of methyl phenyl sulfide.

Run	Conversion (%)[a]	Selectivity (sulfoxide) %
Cycle 1	100	100
Cycle 2	100	100
Cycle 3	100	100
Cycle 4	98	100
Cycle 5	98	100
Cycle 6	95	100
Cycle 7	94	100
Cycle 8	94	100

[a]Reaction conditions: catalyst:sulfide:H_2O_2= 1:80:800 at 25 °C for a 20-min reaction time.

Table 6. Oxidation of various sulfides with H_2O_2 in the presence of CuL-Y.[a]

Substrates	Conversion % CuL-Y	Selectivity % (Sulfoxide) (CuL-Y)
	100	100
	97	90
	100	100
	93	95
	55	100
	100	100
	100	100
	95	100
	100	100
	100	100

[a]Reaction conditions: catalyst:sulfide:H_2O_2= 1:80:800 at 25 °C for a 20-min reaction time.

Table 7. The effect of various conditions on the oxidation of cyclooctene catalyzed by CuL-Y.

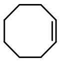
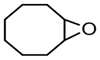
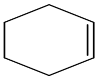
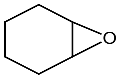
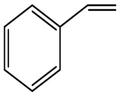
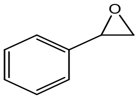
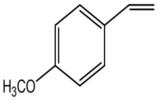
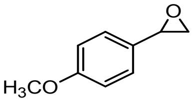
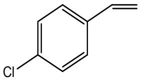
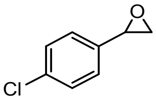
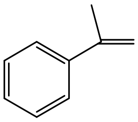
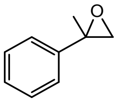
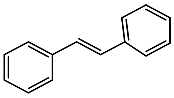
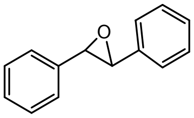
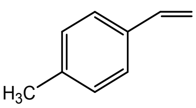
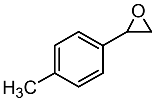
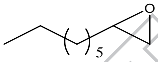
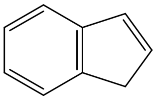
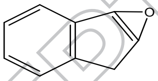
Entry	Time (h)	Temperature (ºC)	Oxidant	Alkene/oxidant	Conversion (%)	Selectivity Epoxide%	Solvent	Catalyst (g)
1	4	25	H_2O_2	1:1	15	100	EtOH	0.009
2	4	25	H_2O_2	1:2	24	100	EtOH	0.009
3	4	25	H_2O_2	1:3	29	100	EtOH	0.009
4	4	25	H_2O_2	1:4	36	100	EtOH	0.009
5	4	25	H_2O_2	1:5	41	100	EtOH	0.009
6	4	25	H_2O_2	1:10	91	100	EtOH	0.009
7	4	25	H_2O_2	1:10	21	100	$CHCl_3$	0.009
8	4	25	H_2O_2	1:10	84	100	CH_3CN	0.009
9	4	25	H_2O_2	1:10	27	100	CH_2Cl_2	0.009
10	1	25	H_2O_2	1:10	41	100	EtOH	0.009
11	1	35	H_2O_2	1:10	70	100	EtOH	0.009
12	1	50	H_2O_2	1:10	94	100	EtOH	0.009
13	1	55	H_2O_2	1:10	100	100	EtOH	0.009
14	1	55	H_2O_2	1:10	69	100	EtOH	0.006
15	1	55	H_2O_2	1:10	38	100	EtOH	0.003
16	1	55	H_2O_2	1:10	9	100	EtOH	0

Table 8.Reuse of the heterogeneous catalysts in the oxidation of cyclooctene.

Run	Conversion (%)[a]	Selectivity %
Cycle 1	100	100
Cycle 2	100	100
Cycle 3	100	100
Cycle 4	100	100
Cycle 5	97	100
Cycle 6	95	100
Cycle 7	94	100
Cycle 8	91	100

[a]Reaction conditions: catalyst(mmol):alkene:H_2O_2 is 1:50:500 at 55 °C for a 1-h reaction time.

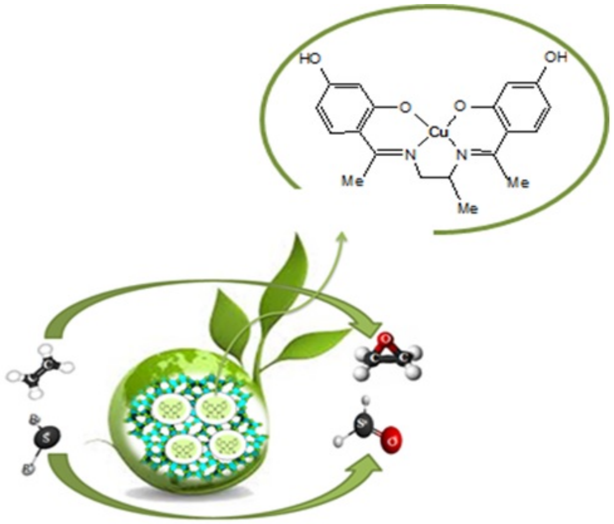
Table 9. Epoxidation of olefins using H_2O_2 catalyzed by CuL-Y in EtOH.[a]

Substrate	Products	Conversion % (CuL_1-Y)	Epoxide selectivity (%) (CuL_1-Y)
		100	100
		100	100
		100	95
		98	94
		97	95
		100	90
		100	100
		100	98
		78	100
		100	100

[a] The molar ratio of catalyst:alkene:H_2O_2 was 1:50:500 in EtOH at 55°C for a 1-h reaction time.

Table 10. Comparison of the catalytic activity of Schiff base complexes encapsulated in zeolite-Y in the oxidation of cyclooctene.

Entry	Catalyst	Solvent	Oxidant	Conversion% (Selectivity, %)	Ref.
1	MnL-Y	CH_3CN	TBHP	88(87)	31
2	MnL1-Y	CH_3CN	H_2O_2	31(100)	25
4	CuL-NaY	CH_3CN	TBHP	48(75)	32
5	CuL_1-Y	EtOH	H_2O_2	100(100)	This work


HO
OH
O
O
Cu
N
N
Me
Me
Me