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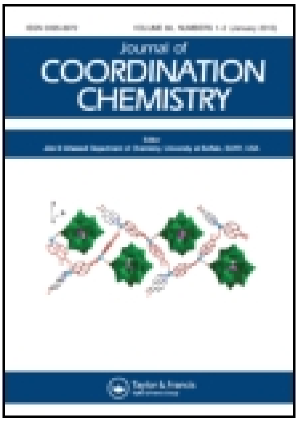

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Epoxidation of cyclooctene by host (nanocavity of zeolite-Y) guest (copper(II) complexes with 16- and 17-membered diaza dioxa macrocyclic Schiff bases) nanocomposite materials

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Epoxidation of cyclooctene by host (nanocavity of zeolite-Y) guest (copper(II) complexes with 16- and 17-membered diaza dioxa macrocyclic Schiff bases) nanocomposite materials

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This work reports the synthesis and characterization of macrocyclic copper(II) complexes encapsulated within the nanopores of zeolite-Y. The obtained nanoparticles entrapped in the nanopores of zeolite have been characterized by FT-IR, UV–Vis, Diffuse reflectance spectra, spectroscopic techniques, molar conductance, magnetic moment data, XRD, thermal, and elemental analysis. The complexes (neat and encapsulated) were used for the oxidation of cyclooctene with tert-butyl hydroperoxide as oxidant in different solvents. The supported $Cu[L_1]^{2+}$-Y exhibited a moderate 81.9% selectivity for epoxidation with 84.2% conversion. The catalytic activity and selectivity of the heterogeneous catalysts do not change after recycling five times.

Keywords: Nanoporous material; Epoxidation of cyclooctene; Copper(II); Schiff base; Macrocycle

1. Introduction

Epoxides are among the most widely used intermediates in organic synthesis, pharmaceuticals as well as polymer production, acting as precursors for complex molecules due to the strained oxirane ring [1], providing detergents, surfactants, antistatic agents, corrosion protection agents, textiles, lubricating oils, and cosmetics [2]. Thus, epoxidation is an important transformation undergone by alkenes. The use of transition metal complexes as catalysts for this reaction has been the subject of interest [3], oxidation being carried out by using oxidants, such as oxygen, hydrogen peroxide, and tert-butyl hydroperoxide (TBHP) [4].

Heterogenization of homogeneous catalysts onto solid supports has been studied because of the long catalytic lifetime, easy separation, thermal stability, high selectivity, and easy recyclability [5, 6]. Many different solid catalysts such as metal oxides [7], zeolites [8], and aluminophosphates [9] can be used to heterogenize homogeneous catalysts. Mixed metal exchanged zeolite, ion exchange resins [10], and polymerized complexes [11] have been used in liquid phase epoxidation of olefins [12]. Recent trends in immobilization of catalyst complexes on clay-based materials such as montmorillonite, zeolites, and bentonite heterogenize homogeneous catalysts [13, 14]. Encapsulation of transition metal complexes in nanopores of zeolite has potential as biomimetic heterogeneous catalysts for oxidation [15, 16].

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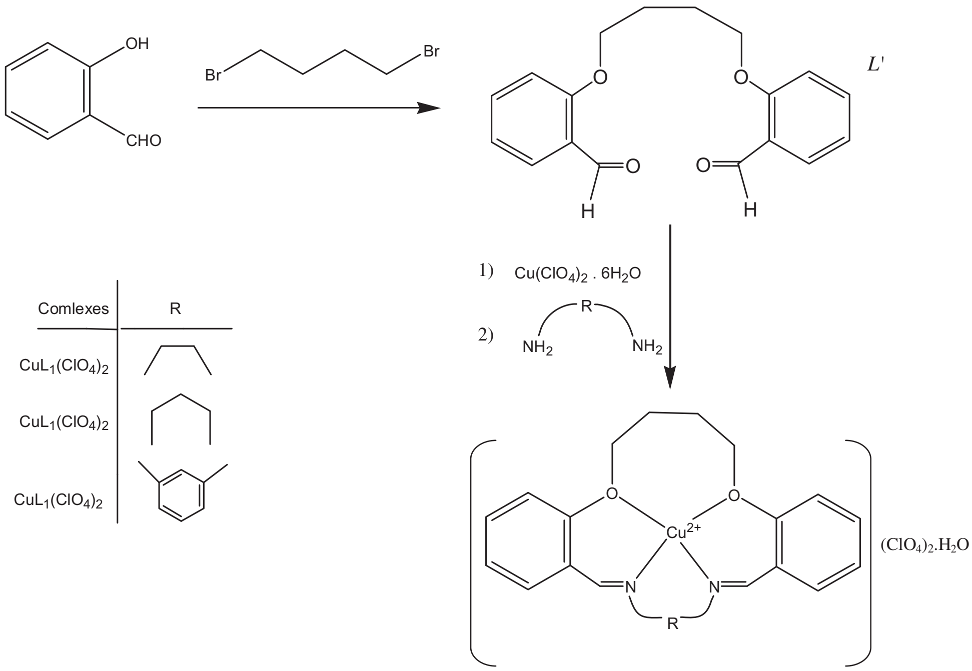


Scheme 1. Preparation of $CuL_1(ClO_4)_2$, $CuL_2(ClO_4)_2$ and $CuL_3(ClO_4)_2$.

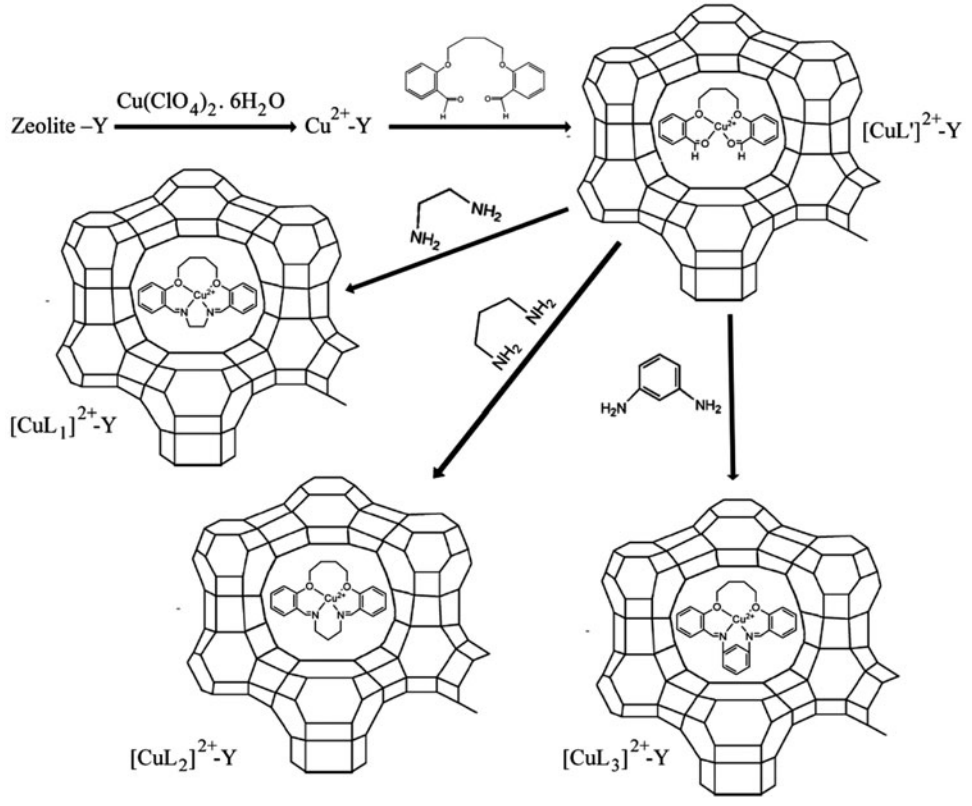
In this article, we report the synthesis and characterization of copper(II) complexes of 16- and 17-membered diaza dioxa macrocycles [L_1]; 3,4,11,12-dibenzo-1,14-diaza-5,10-dioxa cyclohexadecane-1,13-diene, [L_2]; 3,4,11,12-dibenzo-1,14-diaza-5,10-dioxacycloheptadecane-1,13-diene, and [L_3]; 3,4,11,12,15,16,17-tribenzo-1,14-diaza,5,10-dioxa cycloheptadecane-1,13-diene; encapsulated within the nanopores of zeolite-Y by template condensation of diamine and 1,4-bis(2-carboxyaldehydephenoxy)butane [L′]; $Cu[L_1]^{2+}$-Y, $Cu[L_2]^{2+}$-Y and $Cu[L_3]^{2+}$-Y, shown in schemes 1 and 2, and used in the epoxidation of cyclooctene with TBHP as oxygen donor.

2. Experimental

2.1. *Materials and physical measurements*

All materials were of commercial grade with the highest purity and used as received. Solvents used were purified using known procedures. 1,2-Ethylenediamine, 1,3-propanediamine, and 1,3-benzenediamine were purchased from Merck. Cyclooctene and cyclooctene epoxide were purchased from Aldrich chemical company. Na-Y with Si : Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812).

FT-IR spectra were recorded on a Shimadzu Varian 4300 Spectrophotometer in KBr pellets. Electronic spectra of the neat complexes were taken on a Shimadzu UV–Vis scanning spectrometer (Model 1601 PC). Diffuse reflectance spectra (DRS) were recorded on a Scinco 4100 from 200–1100 nm using 6890 series. Elemental analyses (carbon, hydrogen and nitrogen) of the materials were obtained from a Carlo ERBA model EA 1108 analyzer. XRD patterns were recorded by a Rigaku D-Max C III, X-ray diffractometer using



Scheme 2. Encapsulation of copper(II) complex nanoparticles of 16- and 17-membered diaza dioxa Schiff base within nanopores of zeolite-Y.

Ni-filtered Cu Kα radiation. The metal contents were measured by an atomic absorption spectrophotometer (AAS-Perkin–Elmer 4100-1319) using a flame approach. After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum, and copper were analyzed by AAS and SiO_2 was determined by gravimetric analysis.

The products were analyzed by GC and GC-Mass spectra using a 6890 series, FID detector, HP-5% 5-phenyl siloxane and Agilent 5973 network, mass selective detector, HP, 5MS 6890 network GC system.

2.2. *Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane [L']*

To a stirred solution of salicylaldehyde (6.6 g, 50 mM) and K_2CO_3 (12.2 g, 100 mM) in DMF (60 mL) was added dropwise 1,4-dibromobutane (10.8 g, 50 mM) in DMF (20 mL). The reaction was continued for 10 h at 150 °C and then for 5 h at room temperature. Then, 150 mL of distilled water was added and the mixture was put in the refrigerator. One hour later the precipitate was filtered and washed with 300 mL of water, dried in air, recrystallized from ethanol, and dried in vacuum. Yield: 11.3 g (76%), m.p: 105 °C, Color: bright brown. IR (KBr, $\nu\,\mathrm{cm}^{-1}$): 1677 ν(C = O), 1488, 1462 ν(Ar–C = C), 1285, 12.3 ν(Ar–O), 1170, 1040 ν(R–O). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.54; H, 6.06. Found: C, 72.62; H, 6.15.

2.3. *Preparation of $CuL_1(ClO_4)_2$, $CuL_2(ClO_4)_2$ and $CuL_3(ClO_4)_2$*

To a stirred solution of L′ [1,4-bis(2-carboxyaldehydephenoxy)butane] (3.6 g, 12 mM) and $Cu(ClO_4)_2 \cdot 6H_2O$ (4.44 g, 12 mM) in methanol (100 mL), various diamines (12 mM) in methanol (60 mL) were added dropwise. After the addition was completed the stirring was continued for another 2 h. Then the precipitate was filtered, washed with methanol, and dried in air. The products were crystallized from methanol.

2.3.1. $CuL_1(ClO_4)_2 \cdot H_2O$.

Anal. Calcd for $C_{20}H_{24}O_{11}Cl_2N_2Cu$: C, 39.96; H, 3.74; N, 4.52; Cu, 10.67; C/N, 8.84. Found: C, 39.83; H, 3.65; N, 4.64; Cu, 10.54; C/N, 8.58. IR (KBr, $\nu\,cm^{-1}$): 1616 [$\nu_{C=N}$], $\Lambda_M = 160\,\Omega^{-1}\,cm^2\,M^{-1}$ (in DMF), UV–Vis (λ_{max} nm) (in DMF): 225, 264, 312, 550, $\mu_{eff} = 1.91$ BM.

2.3.2. $CuL_2(ClO_4)_2 \cdot H_2O$.

Anal. Calcd for $C_{21}H_{26}O_{11}Cl_2N_2Cu$: C, 40.96; H, 4.35; N, 4.64; Cu, 10.43; C/N, 9.20. Found: C, 40.87; H, 4.22; N, 4.54; Cu, 10.43; C/N, 9. IR (KBr, $\nu\,cm^{-1}$): 1617 [$\nu_{C=N}$], $\Lambda_M = 167\,\Omega^{-1}\,cm^2\,M^{-1}$ (in DMF), UV–Vis (λ_{max} nm) (DMF): 235, 270, 309, 643, $\mu_{eff} = 1.71$ BM.

2.3.3. $CuL_3(ClO_4)_2 \cdot H_2O$.

Anal. Calcd for $C_{24}H_{24}O_{11}Cl_2N_2Cu$: C, 44.25; H, 4.07; N, 4.14; Cu, 9.85; C/N, 10.68. Found: C, 44.14; H, 3.98; N, 4.29; Cu, 9.73; C/N, 10.28. IR (KBr, ν cm^{-1}): 1616 [$\nu_{C=N}$], $\Lambda_M = 161$ $\Omega^{-1}\,cm^2\,M^{-1}$ (in DMF), UV–Vis (λ_{max} nm) (DMF): 221, 271, 344, 458, $\mu_{eff} = 1.73$ BM.

2.4. *Preparation of Cu(II)-Y*

About 5 g of Na-Y zeolite was suspended in 300 mL of distilled water which contained $Cu(ClO_4)_2 \cdot 6H_2O$ (6.93 g, 18.75 mM). The mixture was then heated while stirring at 90 °C for 24 h. The solid was then filtered, washed with hot distilled water till the filtrate was free from any copper(II) ion (by AAS of filtrate) content, and dried for 10 h at 80 °C under vacuum. The ionic exchange degree was determined by an atomic absorption spectrophotometer.

2.4.1. Na-Y.

Anal. Found: Si, 21.58; Al, 8.64; Na, 7.45; Si/Al, 2.53.

2.4.2. Cu(II)-Y.

Anal. Found: Si, 21.56; Al, 8.52; Na, 4.42; Cu, 4.36; Si/Al, 2.53.

2.5. *Preparation of CuL′-Y*

Typically 10 g of Cu(II)-Y zeolite was mixed with 4 g of L′ suspended in 200 mL of methanol and then refluxed for 8 h. The solid consisting of L′ coordinated with Cu(II) in Cu(II)-Y and denoted as $[CuL']^{2+}$-Y was collected by filtration and washed with methanol. The solid was Soxhlet extracted with chloroform (for 4 h) and then with ethanol (for 4 h). The resulting solids were dried at 100 °C under vacuum for 24 h.

2.6. *Preparation of $[CuL_1]^{2+}$-Y, $[CuL_2]^{2+}$-Y and $[CuL_3]^{2+}$-Y*

To a stirred methanol suspension (200 mL) of $[CuL']^{2+}$-Y (4 g) was slowly added diamine, 1,2-diaminobutane, 1,3-diaminopropane or 1,3-diaminobenzene (under N_2). The mixture was heated under reflux for 24 h, filtered, and the resulting zeolite-Y Soxhlet extracted with chloroform (for 4 h) and then with ethanol (for 4 h). The resulting solids were dried at 70 °C under vacuum for 12 h. The remaining $[CuL']^{2+}$ ions in zeolite-Y were removed by exchanging with aqueous 0.01 M NaCl solution.

2.6.1. $[CuL_1]^{2+}$-Y. Anal. Found: C: 11.29, H: 1.26, N: 1.30, C/N: 8.68. Si: 21.21, Al: 8.38, Na: 5.39, Cu: 2.98, Si/Al: 2.53. IR (KBr, $\nu\,cm^{-1}$): 1617 [$\nu_{C=N}$], DRS (λ_{max} nm): 268, 318, 553.

2.6.2. $[CuL_2]^{2+}$-Y. Anal. Found: C: 11.73, H: 1.22, N: 1.27, C/N: 9.23. Si: 21.22, Al: 8.36, Na: 5.37, Cu: 2.94, Si/Al: 2.53. IR (KBr, $\nu\,cm^{-1}$): 1618 [$\nu_{C=N}$], DRS (λ_{max} nm): 265, 305, 633.

2.6.3. $[CuL_3]^{2+}$-Y. Anal. Found: C: 13.39, H: 1.16, N: 1.28, C/N: 10.46. Si: 21.19, Al: 8.37, Na: 5.31, Cu: 2.92, Si/Al: 2.53. IR (KBr, $\nu\,cm^{-1}$): 1617 [$\nu_{C=N}$], DRS (λ_{max} nm): 267, 337, 454.

2.7. *General procedure for catalytic epoxidation of cyclooctene*

A mixture of 5×10^{-2} mM of catalyst and 20 mM cyclooctene in 5 mL CH_3CN was stirred under nitrogen reflux for 30 min. Then 24 mM of TBHP was added and the mixture was refluxed for 4 h. The products were identified by GC–MS. After filtration (heterogeneous catalysts) the solid was washed with acetonitrile. The filtrate was then injected to GC analysis. Internal standard 1,2-dichlorobenzene was used for cyclooctene.

3. Results and discussion

3.1. *Synthesis and characterization of neat complexes*

Reaction between 1,4-bis(2-carboxyaldehydephenoxy)butane, copper(II) perchlorate, and amines in methanol gives the [1 + 1] macrocycle Schiff-base complexes as the major product. The macrocyclic complexes were characterized by elemental analysis, UV, and IR spectrometry. The molecular formulas of the complexes are assigned on the basis of elemental analyses.

A strong band in the IR spectra of the Cu(II) metal complexes at 1616 cm^{-1} is attributed to (C = N) stretch, indicating coordination of the azomethine nitrogen to copper [17]. Broad bands at 3350 cm^{-1} for all complexes can be attributed to stretching vibrations of water [18]. A new band at ~1200 cm^{-1} was assigned to (R–O) [19]. Conclusive evidence of the bonding is also shown by new bands in IR spectra of the Cu(II) metal complexes at 490 and 470 cm^{-1} assigned to (Cu–O) and (Cu–N) stretches [20]. Infrared spectra of the copper(II) complexes exhibit an intense band between 1182 and 1110 cm^{-1} along with a weak band between 651 and 625 cm^{-1} assigned to perchlorate complexes due to *v*(Cl–O) of uncoordinated perchlorate [21].

The metal/ligand mole ratio was 1 : 1, according to elemental analysis. Magnetic moments of the Cu(II) complexes at room temperature range from 1.73–1.91 BM, typical for mononuclear Cu(II) complexes with a S = 1/2 spin-state. The Cu(II) metal complexes are in the ratio of 2 : 1 electrolytes as shown by their molar conductivities (Λ_M) in DMF at 10^{-3} M, which are 160–167 Ω^{-1} cm^2 M^{-1}. The molar conductivities of the compounds in DMF are in the range reported for 2 : 1 electrolytes [17] (scheme 1).

Electronic absorption spectra of all the complexes were recorded in DMF. The absorption bands below 300 nm are identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine. The absorption observed at ~310 nm is probably due to the $\pi \rightarrow \pi^*$ transitions of imines [22]. Electronic spectra also show absorption at 454–643 nm attributed to d–d transitions, characteristic for tetragonally elongated octahedral or square planar geometry [23]. The energy of the band assigned to d–d transitions provides a rough estimate of the ligand field strength.

3.2. *Synthesis and characterization zeolite-Y encapsulated complexes*

Copper(II) complex is encapsulated in the nanopores of zeolite-Y by the reaction of $[Cu(L')]^{2+}$-Y with diamine (1,2-diaminoethane, 1,3-diaminopropane, 1,3-diaminobenzene). Soxhlet extraction using ethanol and chloroform purified the impure complexes. The remaining uncomplexed metal ions in zeolite-Y were removed by exchanging with aqueous 0.01 M NaCl solution. The parent Na-Y zeolite has Si/Al molar ratio of 2.53 which corresponds to a unit cell formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. Initial metal loading in the zeolite lattice is 4.36%, whereas the metal contents are considerably lower in zeolite-Y complexes. This decrease in metal content is attributed to the formation of complexes inside the cavities. CHN analyses of the neat copper complexes are similar to theoretical values. Copper contents of the zeolite-Y encapsulated samples were estimated by dissolving known amounts of the catalyst in concentrated HCl and using AAS. The analytical data of each complex indicate molar ratios of Cu : C : H, close to those calculated for the mononuclear structure.

The IR spectrum of encapsulated complexes show major bands at 2980 cm^{-1} and 1616 cm^{-1} which are absent in the zeolite-Y. IR bands of all encapsulated complex nanoparticles were weak due to their low concentration in zeolite-Y. Cu(II) complex nanoparticles encapsulated in the zeolite cages did not show any significant shift in C = N stretch. We did not notice any appreciable changes in the frequencies of copper(II) complexes after incorporation into zeolite matrix. A comparison of the FT-IR spectra of the encapsulated complex with that of the neat complex indicates the presence of the complex inside the zeolite-Y cage (figure 1).

Comparison of the electronic spectral data of the encapsulated complexes in zeolite-Y and neat complexes confirmed incorporation of Cu(II) complex into the zeolite-Y supercages. The electronic spectral profiles of $[CuL_3]^{2+}$-Y and $(CuL_3)(ClO_4)_2 \cdot H_2O$ are reproduced in Supplemenatry material.

The X-ray diffraction (XRD) patterns of encapsulated complexes are shown in figure 2. The encapsulated complex exhibits similar peaks to those of zeolite-Y, except for a slight change in intensity of the peaks, no new crystalline pattern emerges, confirming that the framework and crystallinity of zeolite were not destroyed during the preparation, and that the complexes were well distributed in the cages. The relative peak intensities of the 220, 311, and 331 reflections correlate to the locations of cations. In zeolite-Y, the order of peak

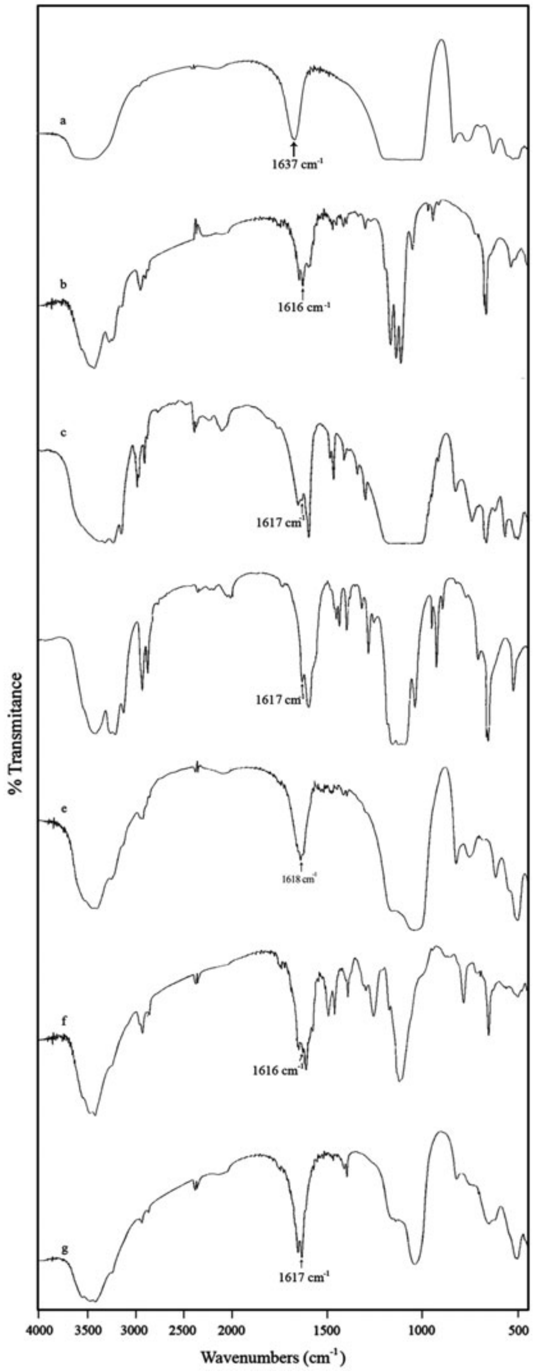


Figure 1. FT-IR spectra: (a) zeolite-Y, (b) $(CuL_1)(ClO_4)_2\cdot H_2O$, (c) $[CuL_1]^{2+}$-Y, (d) $(CuL_2)(ClO_4)_2\cdot H_2O$, (e) $[CuL_2]^{2+}$-Y, (f) $(CuL_3)(ClO_4)_2\cdot H_2O$, (g) $[CuL_3]^{2+}$-Y.

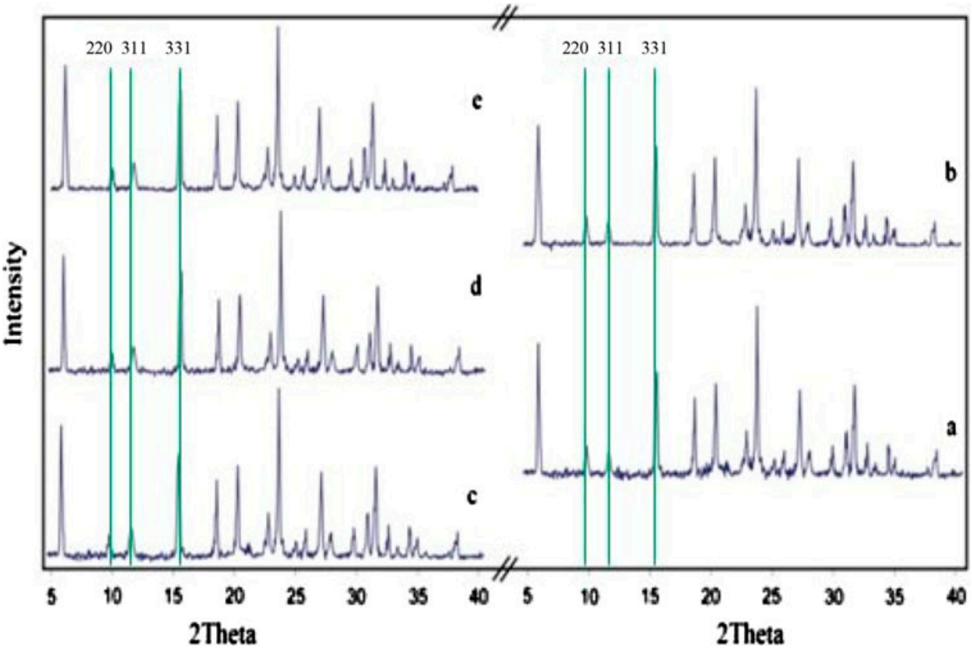


Figure 2. XRD patterns of (a) Na-Y, (b) Cu^{2+}-Y, (c) $[CuL_1]^{2+}$-Y, (d) $[CuL_2]^{2+}$-Y, (e) $[CuL_3]^{2+}$-Y.

intensity is in the order: $I_{331} > I_{220} > I_{311}$, while in encapsulated complexes, the order of peak intensity became $I_{331} > I_{311} > I_{220}$. The difference indicates that the ion-exchanged Cu^{2+}, which substitutes at the location of Na^+, undergoes rearrangement during complexation.

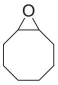
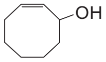
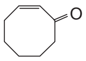
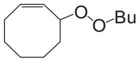
The thermal stability of catalysts was studied by TGA; the TGA profile of $[CuL_3]^{2+}$-Y is reproduced in Supplementary Material. The thermal decomposition of these materials occurs in two steps. The endothermic loss in the first step starts above 140 °C and continues until the loss of all intrazeolite water. The exothermic loss in the two steps occurs in a wide temperature range (450–800 °C) due to slow decomposition of the chelating ligand. A very small weight percentage loss indicates the presence of only a small amount of metal complex in the nanopores of zeolite-Y, in agreement with the low percentage of metal content estimated by AAS. The thermal stability of the encapsulated complex is confirmed.

3.3. *Catalytic activity*

Schiff base metal complex-catalyzed oxidation of organic compounds has been extensively reported [24, 25]. Transition metal complex-based soluble catalysts are prone to deactivation by dimerization of active centers which is expected to be reduced by encapsulating them in zeolites [26]. The most important advantage of heterogeneous catalysis over its homogeneous counterpart is increase of complex stability in the reaction medium and the possibility of reusing the catalyst after reaction by simple filtration [27].

The catalytic activities of neat and encapsulated complexes were evaluated for oxidation of cyclooctene with TBHP. The major product of oxidation of cyclooctene is cyclooctane epoxide. The selectivity and activity of zeolite-Y encapsulated and homogeneous catalysts on the epoxidation of cyclooctene with TBHP are shown in table 1.

Table 1. Epoxidation of cyclooctene with TBHP catalyzed by nanopores of zeolite encapsulated and neat copper (II) complexes in CH_3CN. Conditions: catalyst 0.05 mM, TBHP 24 mM, cyclooctene 20 mM, CH_3CN 5 mL, temperature 80 °C.

			Selectivity (%)			
Catalyst	Time (h)	Conversion (%)				
Cu(II)-Y	6	23.4	23.4	24.8	45.6	6.2
$[Cu(L_1)]^{2+}$-Y	2	61.3	71.1	19.1	6.6	2.2
$[Cu(L_1)]^{2+}$-Y	4	81.3	80.2	11.5	6.4	1.9
$[Cu(L_1)]^{2+}$-Y	6	83	82.3	9.3	5.9	2.5
$[Cu(L_1)]^{2+}$-Y^a	8	84.2	81.9	9.5	6	2.6
$[Cu(L_1)]^{2+}$-Y^b	8	83.7	82.5	9.4	5.7	2.4
$[Cu(L_1)]^{2+}$-Y^c	8	84.1	81.3	9.9	6.1	2.7
$[Cu(L_2)]^{2+}$-Y	2	51.3	71.3	18.7	7.5	2.5
$[Cu(L_2)]^{2+}$-Y	4	73.4	71.9	19.7	7.1	2.3
$[Cu(L_2)]^{2+}$-Y	6	74.8	72.8	18.3	5.6	3.3
$[Cu(L_2)]^{2+}$-Y^a	8	75.5	73.2	18.1	5.5	3.2
$[Cu(L_2)]^{2+}$-Y^d	8	75	73.9	18.3	4.9	2.9
$[Cu(L_2)]^{2+}$-Y^f	8	74.8	72.5	18.7	5.3	3.5
$[Cu(L_3)]^{2+}$-Y	2	53.7	63.1	29.2	5.6	2.1
$[Cu(L_3)]^{2+}$-Y	4	68.9	65.3	27.6	4.8	2.3
$[Cu(L_3)]^{2+}$-Y	6	71.2	68.8	22.1	6.1	3
$[Cu(L_3)]^{2+}$-Y^a	8	72.3	69.7	21.7	5.8	2.8
$[Cu(L_3)]^{2+}$-Y^c	8	72.1	70.3	21.4	5.2	3.1
$[Cu(L_3)]^{2+}$-Y^f	8	71.8	69.5	21.4	5.6	3.5
$CuL_1(ClO_4)_2 \cdot H_2O$	4	70.8	70.2	23.2	4.2	2.4
$CuL_2(ClO_4)_2 \cdot H_2O$	4	59.9	64.7	27.4	5.3	2.6
$CuL_3(ClO_4)_2 \cdot H_2O$	4	56.6	61	28.7	7.1	3.2

[a]First reuse. [b]Second reuse. [c]Third reuse. [d]Fourth reuse. [f]Fifth reuse.

Comparing neat and encapsulated complexes shows that zeolite-Y encapsulated catalysts gave higher conversion of cyclooctene than their corresponding neat complexes. The higher activity of supported complexes is because of site isolation of the complexes.

We examined reaction times of 2, 4, 6, and 8 h. The results are shown in table 1. At 4 h maximum conversion takes place and longer times have no effect on reactivity. The observation of a plateau after 4 h is not unexpected because cyclooctene is depleted.

To investigate the role of solvent on the reaction and product distribution, we carried out the reaction in protic and aprotic solvents. The results are given in tables 1–3. Polar aprotic solvent such as acetonitrile is particularly efficient in providing both high cyclooctene conversion and high-epoxide selectivity.

The zeolite-Y encapsulated complexes did not undergo any color change during the reaction and could be separated and reused many times without major loss in activity. The catalytic activity and selectivity of heterogeneous catalysts have not changed after five times of reusing (figure 3 and table 1). In contrast, the neat complexes were completely destroyed during the first run and changed color. Thus, the encapsulation of complexes in

Table 2. Epoxidation of cyclooctene with TBHP catalyzed by nanopores of zeolite encapsulated copper(II) complexes in CH_3OH. Conditions: catalyst 0.05 mM, TBHP 24 mM, cyclooctene 20 mM, CH_3OH 5 mL, temperature 80 °C.

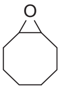
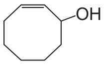
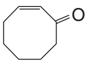
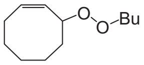
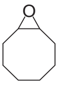
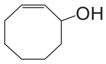
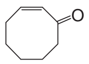
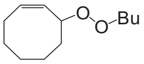
			Selectivity (%)			
Catalyst	Time (h)	Conversion (%)				
$[CuL_1]^{2+}$-Y	4	70.5	65.8	26.9	3.9	3.4
$[CuL_2]^{2+}$-Y	4	63.2	56.3	36.6	4.2	2.8
$[CuL_3]^{2+}$-Y	4	61.5	55.2	38.9	3.5	2.4

Table 3. Epoxidation of cyclooctene with TBHP catalyzed by nanopores of zeolite encapsulated copper(II) complexes in CH_2Cl_2. Conditions: catalyst 0.05 mM, TBHP 24 mM, cyclooctene 20 mM, CH_3OH 5 mL, temperature 80 °C.

			Selectivity (%)			
Catalyst	Time (h)	Conversion (%)				
$[CuL_1]^{2+}$-Y	4	55.3	62.4	20.4	12.5	4.7
$[CuL_2]^{2+}$-Y	4	53.8	55.8	27.9	11.2	5.1
$[CuL_3]^{2+}$-Y	4	50.2	50.8	34	9.3	5.9

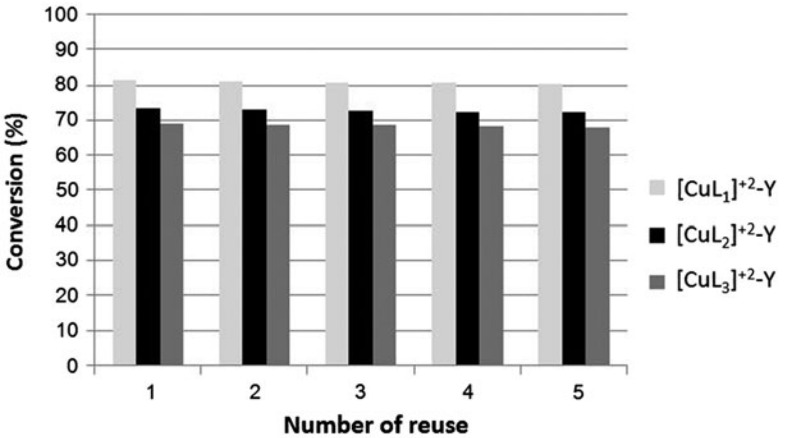


Figure 3. The catalytic activity of the zeolite encapsulated copper (II) complexes in 5 runs of cyclooctene epoxidation (catalyst 0.05 mM, TBHP 24 mM, cyclooctene 20 mM, CH_3CN 5 mL, time 4 h, 80 °C).

zeolites increases the life of the catalyst by reducing dimerization due to the restriction of internal framework structure.

Epoxidation of cyclooctene with TBHP over copper Schiff base catalysts under heterogeneous conditions has been studied. According to our results, expoxidation of cyclooctene was carried out with 84.2% conversion and 81.9% selectivity (see table 1 and figure 4).

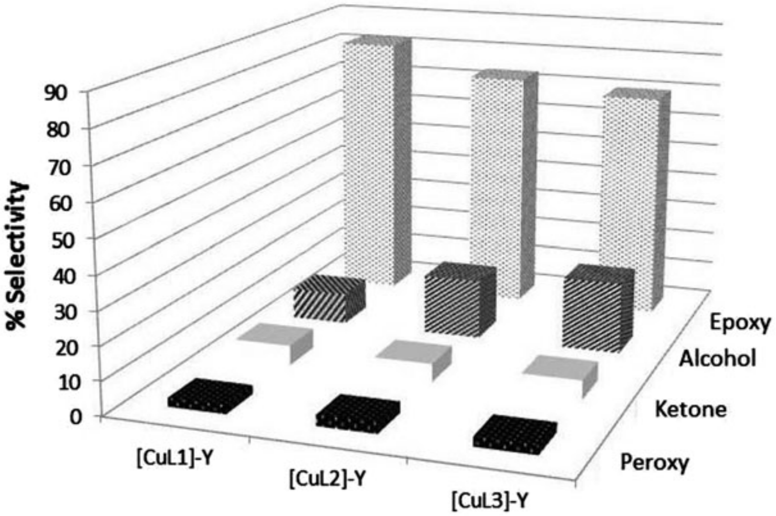


Figure 4. Product selectivity for oxidation of cyclooctene catalyzed by heterogeneous Cu(II) complexes at 0.05 mM, TBHP 24 mM, cyclooctene 20 mM, CH_3CN 5 mL, time 4 h, 80 °C.

As compared to the recently published system with Cu-salen immobilized on MCM-41 and MCM-48 giving 53–54% conversion of cyclooctene with 78–85% epoxide selectivity, our system seems simpler, more economical, and more efficient [28].

4. Conclusion

Copper(II) complexes with 16- and 17-membered diaza dioxa Schiff base macrocyclic ligands have been encapsulated in nanopores of zeolite-Y. The resulting catalysts have been spectroscopically characterized (IR, DRS, UV–Vis), elemental analysis, etc. This catalytic system showed high activity in epoxidation of cyclooctene under mild reaction conditions. Encapsulated complexes can be recovered and reused without loss of catalytic activity. As compared to the recently published system which worked with Mn-hydrazone Schiff base immobilized on zeolite-Y, our system seems competitive [29].

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