



Synthesis, characterization of cobalt(II) complex nanoparticles encapsulated within nanoreactors of zeolite-Y and their catalytic activities

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ABSTRACT

Cobalt(II) complex nanoparticles of [14]aneN₄: 1,5,8,12-tetraaza-2,9-dioxo-4,11-diphenylcyclotetradecane; [16]aneN₄: 1,5,9,13-tetraaza-2,10-dioxo-4,12-diphenylcyclohexadecane; Bzo₂[14]aneN₄: dibenzo-1,5,8,12-tetraaza-2,9-dioxo-4,11-diphenylcyclotetradecane and Bzo₂[16]aneN₄: dibenzo-1,5,9,13-tetraaza-2,10-dioxo-4,12-diphenylcyclohexadecane have been encapsulated in the nanopores of zeolite-Y by a two-step process in the liquid phase: (i) adsorption of [bis(diamine)cobalt(II)] (diamine = 1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene); [Co(N-N)₂]²⁺-NaY; in the nanopores of the zeolite-Y, and (ii) in situ condensation of the cobalt(II) precursor complex with ethylcinnamate. The new complex nanoparticles entrapped in the nanoreactor of zeolite-Y were characterized by several techniques: BET, chemical analysis and spectroscopic methods (FT-IR, UV-vis, XRD, and DRS). These complexes (neat and encapsulated) were used for epoxidation of styrene with O₂ as oxidant in different solvents. Electronic spectra of the reaction mixture indicated that the oxidation proceeds through a free radical mechanism.

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1. Introduction

Increasingly restrictive regulations concerning environment protection induce progress in the technology of chemical processes. This is why there is a growing interest in homogeneous catalysts like enzymes. Enzymes are natural catalysts, well-known for their high selectivity, operating at mild temperatures but their use in an industrial environment is expensive and their handling and manipulation are rather difficult. On the other hand, the traditional heterogeneous catalysts which are rather robust can operate under more severe conditions and have generally good stability and are manufactured at relatively low costs. But in comparison with the enzymes, their selectivity in most cases is significantly lower. The advantages of both systems can be combined and the disadvantages can be eliminated by the immobilization of homogeneous catalysts, e.g. enzymes on the surface of heterogeneous supports. The immobilization of transition metal complexes on different supports seems to be a good method to satisfy environmental demands and to obtain catalysts which preserve the properties of homogeneous systems but they are more stable and can be easily recovered.

Nanopores structures are attractive matrixes for immobilization of transition metal complexes which are known to be active in homogeneous catalysis. Especially, the three-dimensional large pore zeolites (X and Y) have been studied as host lattices. The encapsulated complex is too bulky to move away from a large cage or a channel crossing the term ship-in-a-bottle system applies [1–10]. The isolated complex immobilized in this way has special properties. It is unable to undergo transformations, which sometimes are deactivating processes in homogeneous catalysis. Moreover, when it is formed in the zeolite voids, the complex may have a unique configuration which may differ from the configuration existing in solution and acquire new catalytic properties. Finally, the surrounding zeolite may have a bearing on the selectivity in parallel reactions by influencing in a different way the transition states in question [11].

Most frequently, inside the large pores of the zeolites metalloporphyrins and their analogues as phthalocyanines, Schiff-bases and macrocyclic [12–21] were prepared. They have been studied extensively as biomimetic catalysts for alkene epoxidation and alkane hydroxylation with variety of oxidants including hydrogen peroxide, hydroperoxides, iodosylbenzenes and hypochlorites [13,14,16–21,22–25]. There are only a few papers on oxidation of hydrocarbons with dioxygen in the presence of zeolite-encapsulated metal complexes as catalysts [26–31].

In this work, the tetraaza ligands and their encapsulated complexes were chosen (Scheme 1) in the epoxidation reaction. So far, encapsulated tetraaza cobalt(II) complexes have not been used

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within the nanopores of zeolite-Y in the epoxidation of styrene. The use of these encapsulated complexes as nanocatalysts can enhance the selectivity in the oxidation reaction. The complex nanoparticles entrapped in the nanoreactor of zeolite-Y can be considered as windows to the selection a suitable nanocatalyst for the oxidation reaction. In this paper, the synthesis and characterization of cobalt(II) complexes of 14- and 16-membered tetraaza macrocyclic ligand have been reported; [14]aneN₄: 1,5,8,12-tetraaza-2,9-dioxo-4,11-diphenylcyclotetradecane; [16]aneN₄: 1,5,9,13-tetraaza-2,10-dioxo-4,12-diphenylcyclohexadecane; Bzo₂[14]aneN₄: dibenzo-1,5,8,12-tetraaza-2,9-dioxo-4,11-diphenylcyclotetradecane and Bzo₂[16]aneN₄: dibenzo-1,5,9,13-tetraaza-2,10-dioxo-4,12-diphenylcyclohexadecane; encapsulated within the nanopores of zeolite-Y by the template condensation of ethylcinnamate and [bis(diamine)cobalt(II)]; [Co([14]aneN₄)]²⁺-NaY, [Co([16]aneN₄)]²⁺-NaY, [Co(Bzo₂[14]aneN₄)]²⁺-NaY, [Co(Bzo₂[16]aneN₄)]²⁺-NaY; shown in Scheme 1 and used in the epoxidation of styrene.

2. Experimental

2.1. Materials

Safety note: Cobalt perchlorate salt with organic ligands is often explosive and should be handled with caution. All other reagents and solvents were purchased from Merck (pro-analysis) and dried using molecular sieves (Linde 4 Å). Styrene was distilled under nitrogen and stored over molecular sieves (4 Å). NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). The complex [Co(N-N)₂](ClO₄)₂ was prepared according to the published procedures [32].

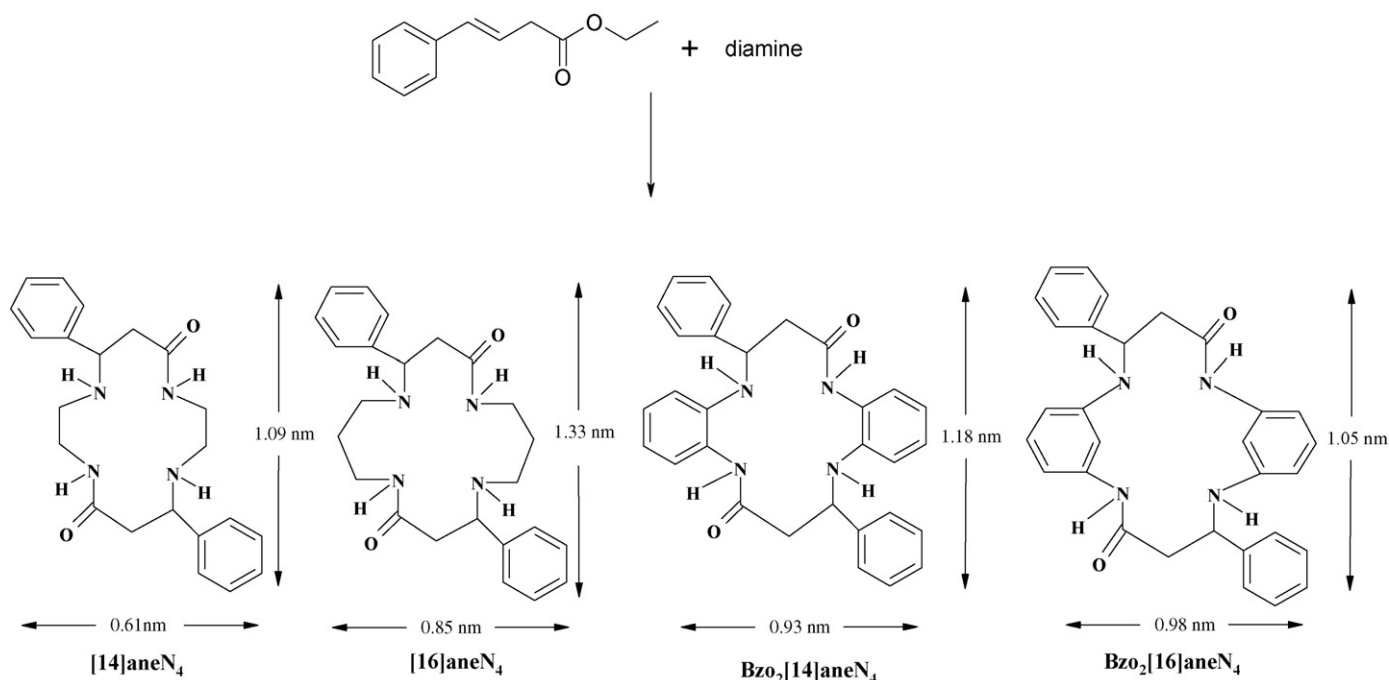
2.2. Physical measurements

The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffrac-

tometer using Ni-filtered Cu K α radiation. Nitrogen adsorption measurements were performed at 77 K using a Coulter Ofeisorb 100CX instrument. The samples were degassed at 150 °C until a vacuum better than 10⁻³ Pa was obtained. Micropore volumes were determined by the *t*-method. A “monolayer equivalent area” was calculated from the micropore volume [33,34]. FAB mass spectra were recorded on a Kratos MS50TC spectrometer. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the neat complexes were taken on a Shimadzu UV-vis scanning spectrometer (Model 2101 PC). The stability of the encapsulated catalyst was checked after the reaction by UV-vis and possible leaching of the complex was investigated by UV-vis in the reaction solution after filtration of the zeolite. The amounts of metallocomplexes encapsulated in zeolite matrix were determined by the elemental analysis and by subtracting the amount of metallocomplex left in the solutions from the amount taken for the synthesis after the synthesis of the catalysts as determined by UV-vis spectroscopy. Atomic absorption spectra (AAS) were recorded on a PerkinElmer 4100-1319 Spectrophotometer using a flame approach after acid (HF) dissolution of known amounts of the zeolitic material and SiO₂ was determined by gravimetric analysis. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 nm, using MgO as reference.

2.3. Synthesis of 14- and 16-membered tetraaza macrocyclic ligands

Tetraaza macrocyclic ligands ([14]aneN₄, [16]aneN₄, Bzo₂[14]aneN₄ or Bzo₂[16]aneN₄) were prepared by following the procedures reported in Ref. [35]. The hot ethanol solution (20 ml) of ethylcinnamate (3.52 g, 0.02 mol), a hot ethanol solution (20 ml) of diamine (0.02 mol), 1,2-diaminoethane (1.20 g), 1,3-diaminopropane (1.48 g), 1,2-diaminobenzene (2.16 g) and 1,3-diaminobenzene (2.16 g) were mixed slowly with constant stirring. This mixture was refluxed at 80 °C for 12 h in presence of few drops of concentrated HCl acid. After cooling, a white precipitate



Scheme 1. The schematic structures of tetraaza macrocyclic ligands.

Table 1
Elemental analysis, vibrations parameters and molecular ion peaks for ligands and tetraaza 14- and 16-membered macrocyclic cobalt(II) complexes.

Sample	Calculated (found)				IR (KBr, cm ⁻¹)								FAB mass (m/z)	
	C (%)	H (%)	N (%)	C/N	Co (%)	I	II	III	IV	ν _{N-H}	ν _{Co-N}	[M-ClO ₄] ⁺	[M-2ClO ₄] ²⁺	
[14]aneN ₄	69.45 (69.28)	7.42 (7.30)	14.72 (14.90)	4.72 (4.65)	–	1624	1593	1249	780	3286	–	–	–	
[Co([14]aneN ₄)](ClO ₄) ₂	41.40 (41.22)	4.42 (4.30)	8.78 (8.90)	4.72 (4.63)	9.23 (9.04)	1626	1592	1247	776	3260	470	538	439	
[16]aneN ₄	70.56 (70.33)	7.89 (7.74)	13.71 (13.88)	5.15 (5.07)	–	1620	1590	1248	780	3280	–	–	–	
[Co([16]aneN ₄)](ClO ₄) ₂	43.26 (43.11)	4.84 (4.70)	8.41 (8.58)	5.14 (5.02)	8.84 (8.69)	1622	1588	1246	779	3256	469	567	467	
Bzo ₂ [14]aneN ₄	75.61 (75.40)	5.92 (5.73)	11.76 (11.84)	6.43 (6.37)	–	1630	1596	1252	782	3290	–	–	–	
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂	49.06 (48.88)	3.84 (3.70)	7.63 (7.80)	6.43 (6.27)	8.02 (7.89)	1635	1595	1250	780	3268	475	635	534	
Bzo ₂ [16]aneN ₄	75.61 (75.43)	5.92 (5.71)	11.76 (11.88)	6.43 (6.35)	–	1627	1594	1250	782	3288	–	–	–	
[Co(Bzo ₂ [16]aneN ₄)](ClO ₄) ₂	49.06 (48.84)	3.84 (3.70)	7.63 (7.78)	6.43 (6.28)	8.02 (7.90)	1632	1593	1252	780	3264	472	635	535	

was formed which was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀. The purity was checked by HPLC technique.

2.4. Preparation of tetraaza cobalt(II) complexes

Cobalt(II) perchlorate hexahydrate (0.01 mol) dissolved in ethanol (20 ml) was reacted with an ethanolic (20 ml) solution of tetraaza ligands ([14]aneN₄, [16]aneN₄, Bzo₂[14]aneN₄ or Bzo₂[16]aneN₄) (0.01 mol) by refluxing for 4 h under nitrogen atmosphere. The mixture was heated at reflux for 6 h until an orange solution resulted. The solution was cooled to room temperature and filtered to remove Co(OH)₂. Excess Li(ClO₄)₃·3H₂O dissolved in MeOH was added to the filtrate, and the mixture was kept in the refrigerator until orange solid was formed. The solids were filtered and washed thoroughly with cold ethanol and was dried in vacuum.

2.5. Preparation of Co(II)–NaY

An amount of 2 g NaY zeolite was suspended in 100 ml distilled water which contained Co(NO₃)₂·6H₂O (0.025 M). The mixture was then heated while stirring at 90 °C for 24 h. The light pink solid was filtered washed with hot distilled water till the filtrate became free from any cobalt(II) ion (by AAS of filtrate) content and then was dried for 10 h at 80 °C under vacuum. The ionic exchange degree was determined by AAS.

2.6. Preparation of [Co(N–N)₂]²⁺–NaY

Typically, a 4-g sample of NaY zeolite was mixed with 0.37 g of [Co(N–N)₂](ClO₄)₂, diamine = 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,3-diaminobenzene suspended in 100 ml of MeOH and the mixture was refluxed for 8 h. The pale orange solid consisting of [Co(N–N)₂]²⁺ exchanged with Na⁺ in NaY and denoted as [Co(N–N)₂]²⁺–NaY was collected by filtration and washed with EtOH. The resulted zeolites were Soxhlet extracted with DMF (for 4 h) and then with EtOH (for 3 h) to remove excess unreacted diamine and any Co(II) complexes adsorbed onto the external surface of the zeolite crystallines. The resulting light orange solids were dried at 60 °C under vacuum for 24 h.

2.7. Preparation of tetraaza cobalt(II) complex nanoparticles entrapped in the nanoreactor of zeolite-Y: [Co([14 or 16]aneN₄)]²⁺–NaY and [Co(Bzo₂[14 or 16]aneN₄)]²⁺–NaY

Ethylcinnamate (0.80 g) was slowly added to a stirred methanol suspension (100 ml) of [Co(N–N)₂]²⁺–NaY (2 g) (under N₂ atmosphere). The mixture was heated under reflux condition for 24 h until a pale orange suspension resulted. The solution was filtered and the resulting zeolites were Soxhlet extracted with DMF (for 6 h) and then with ethanol (for 5 h) to remove excess unreacted products from amine-ester condensation and any cobalt(II) complexes adsorbed onto the external surface of the zeolite crystallines. The

resulting pale orange solids were dried at 70 °C under vacuum for 12 h. The remaining [Co(N–N)₂]²⁺ ions in zeolite were removed by exchanging with aqueous 0.1 M NaCl solutions. The stability of the encapsulated catalyst was checked after the reaction by UV–vis and possible leaching of the complex was investigated by UV–vis in the reaction solution after filtration of the zeolite. The amount of Co(II) complexes encapsulated in zeolite matrix were determined by the elemental analysis and subtracting the amount of Co(II) complex left from the solutions from the amount taken for the synthesis after the synthesis of the catalysts is determined by UV–vis spectroscopy.

2.8. Epoxidation of styrene: general procedure

The epoxidation of styrene with molecular oxygen was carried out with a round-bottomed glass flask reactor. In a typical run, a measured amount of catalyst was added to the reactor which was precharged with the desired amount of reactant and solvent, typically *N,N*-dimethylformamide (DMF), at the desired temperature. The reaction started off under bubbling O₂ or O₂ diluted with N₂ into the liquid. The reactant mixture was stirred vigorously during the reaction. After the reaction, the catalyst was filtered off and the liquid organic products were quantified with a gas chromatograph with toluene as an internal standard.

3. Results and discussion

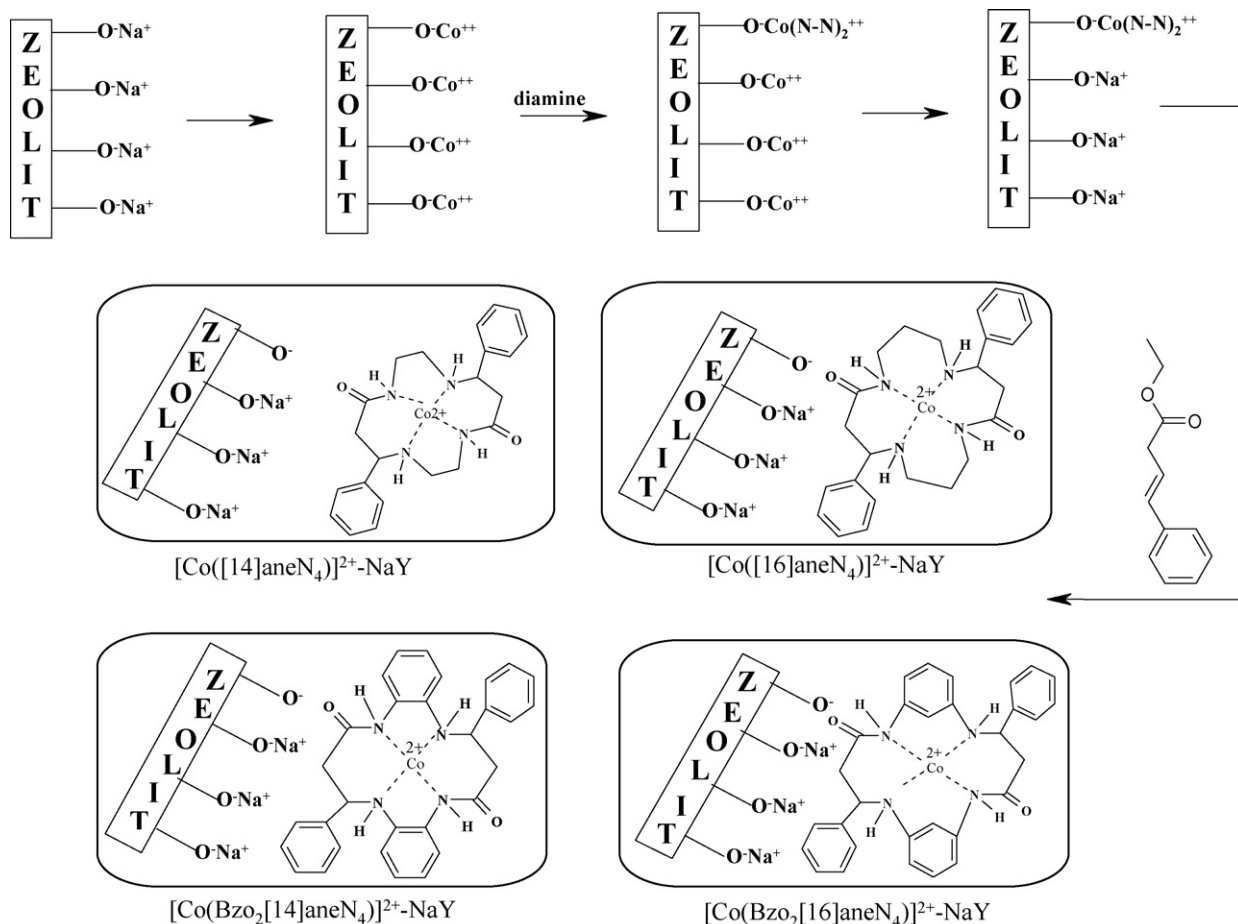
3.1. Synthesis and characterization of “neat” complexes

The molecular formula of the complexes has been assigned on the basis of the results of their elemental analyses and the molecular ion peaks in the mass spectra. All mass spectra showed molecular ion peaks for the 1:1 metal-to-ligand stoichiometry with no further peaks above them (Table 1). A preliminary identification of the metal complexes was made on the basis of their IR spectra which exhibited no bands characteristic of free primary amine which supported the proposed macrocyclic skeleton (Scheme 1). The deep orange complexes “[Co([14 or 16]aneN₄)](ClO₄)₂ and [Co(Bzo₂[14 or 16]aneN₄)](ClO₄)₂” readily dissolve in polar solvents such as H₂O, MeCN, MeNO₂ and DMSO. The cobalt(II) complexes are extremely stable in the solid state and in solution and are relatively stable against ligand dissociation even in highly acidic solutions. The molar conductance values of the com-

Table 2
Magnetic moment, electronic spectral and molar conductance values of the tetraaza macrocyclic cobalt(II) complexes.

Sample	<i>d</i> ↔ <i>d</i> (nm) ^a	μ _{eff} (MB)	Λ _M ^a , Ω ⁻¹ cm ² M ⁻¹
[Co([14]aneN ₄)](ClO ₄) ₂	452	1.80	246
[Co([16]aneN ₄)](ClO ₄) ₂	454	1.78	244
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂	445	1.75	240
[Co(Bzo ₂ [16]aneN ₄)](ClO ₄) ₂	447	1.76	235

^a In nitromethane solutions.



Scheme 2. Cobalt complex nanoparticles entrapped inside zeolite NaY.

plexes ($235\text{--}246\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^2$) measured in H_2O correspond to 1:2 electrolytes. The overall geometries of all macrocycles have been deduced on the basis of the observed values of the magnetic moments and the band positions in the electronic spectra. The magnetic moments ($1.75\text{--}1.80\ \mu_{\text{B}}$) of the Co(II) complexes measured in the solid state correspond to the square-planar coordination geometry of the complexes (Table 2).

IR spectrum of the ligand does not exhibit any band corresponding for the free primary diamine and hydroxyl group. The absorption in IR spectrum of tetraaza in the range of $730\text{--}770$ and $1415\text{--}1645\ \text{cm}^{-1}$ [36] is due to the presence of phenyl group. Four new bands appear in the spectrum of the free ligand in the regions ~ 1620 , ~ 1590 , ~ 1248 , and $\sim 780\ \text{cm}^{-1}$ correspond to amide I [$\nu(\text{C}=\text{O})$], amide II [$\nu(\text{C}-\text{N}) + \delta(\text{N}-\text{H})$], amide III [$\delta(\text{N}-\text{H})$], and amide IV [$\nu(\text{C}=\text{O})$] bands, respectively [37]. A sharp band observed $\sim 3278\ \text{cm}^{-1}$, may be due to [$\nu(\text{N}-\text{H})$] of the secondary amino group [38]. The IR spectra of all the complexes (Table 1) showed a single sharp absorption around $\sim 3260\ \text{cm}^{-1}$ which may possibly arise from a secondary amine, $\nu_{\text{N-H}}$, although its position has been found to be lower by $\sim 20\ \text{cm}^{-1}$ than the analogous metal-free tetraaza ligands [39–41]. This suggests that the secondary amine nitrogen takes part in coordination to the metal ions which has been further confirmed by the appearance of bands in the $469\text{--}475\ \text{cm}^{-1}$ region in all the complexes corresponding to $\nu_{\text{Co-N}}$ vibrations. The absorption bands in the $2850\text{--}3050$ and $1400\text{--}1450\ \text{cm}^{-1}$ regions observed in the complexes may reasonably correspond to C–H stretching and C–H bending vibrational modes. The IR bands of all encapsulated complexes are weak in comparison with the neat complexes due to their low concentrations in zeolite nanocages. The four entrapped complexes exhibit very similar IR spectra with bands at all regions

that are shifted $\sim 3\ \text{cm}^{-1}$ relative to those of the corresponding free complexes.

Comparing the obtained magnetic measurement at room temperature and the results of electronic spectra (Table 2) of metal complexes with square-planer Co(II) tetraaza macrocycle complexes indicated that the tetraaza tetraone ligands of this study do not differ significantly from the tetraaza ligands with respect to the ligand field strength. Bands due to zeolite encapsulated Co(II) complex appeared in the visible region and charge transfer bands appeared in the near-UV region. These values were very similar to the obtained values for the discrete neat complexes [38–43].

3.2. Synthesis and characterization of tetraaza cobalt(II) complex nanoparticles entrapped in the nanoreactor of zeolite-Y

Synthesis of tetraaza cobalt(II) complexes encapsulated in the nanocavity of zeolite-Y involves two steps: (i) exchange of $[\text{Co}(\text{N-N})_2]^{2+}$ (diamine = 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,3-diaminobenzene) ions with NaY in methanol solution and (ii) reaction of $[\text{Co}(\text{N-N})_2]^{2+}\text{-NaY}$ with excess ethylcinnamate in methanol where ethylcinnamate slowly enters into the nanocavity of zeolite-Y due to its template nature and interacts with $[\text{Co}(\text{N-N})_2]^{2+}$ (Scheme 2). Soxhlet extraction using MeOH finally purified the impure complexes. The remaining uncomplexed metal ions in zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. As two extra anionic ligands would be required to balance the overall charges on the Co(II), Cl^- of NaCl used during exchanged process fulfills this requirement. Thus, the formula of cobalt(II) complex may

Table 3Chemical composition, DRS and IR stretching frequencies (as KBr pellets, cm^{-1}) of tetraaza cobalt(II) complex nanoparticles entrapped in the nanoreactor of zeolite-Y.

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Co (%)	Si/Al	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$d \leftrightarrow d$ (nm)
NaY	–	–	–	–	21.76	8.60	7.50	–	2.53	–	–	–
Co(II)–NaY	–	–	–	–	21.53	8.53	3.36	3.71	2.53	–	–	–
[Co([14]aneN ₄)] ²⁺ –NaY	4.30	1.63	0.95	4.53	21.14	8.35	5.27	2.80	2.53	3254	1626	450
[Co([16]aneN ₄)] ²⁺ –NaY	4.32	1.65	0.86	5.01	21.12	8.34	5.25	2.78	2.53	3251	1624	453
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ –NaY	4.36	1.68	0.70	6.20	21.09	8.33	5.22	2.75	2.53	3262	1633	442
[Co(Bzo ₂ [16]aneN ₄)] ²⁺ –NaY	4.35	1.69	0.70	6.23	21.08	8.33	5.23	2.76	2.53	3260	1631	446

be written as [Co([14]aneN₄)]²⁺–NaY, [Co([16]aneN₄)]²⁺–NaY, [Co(Bzo₂[14]aneN₄)]²⁺–NaY, [Co(Bzo₂[16]aneN₄)]²⁺–NaY.

The percentage of metal contents determined before and after encapsulation by inductively coupled plasma (ICP) along with their expected formula has been presented in Table 3. As crude mass was extracted with methanol, the metal ion content found after encapsulation is maybe to the presence of metal complexes in the nanocages of the zeolite-Y. The molecular formula of the complexes are based on the neat complexes [Co([14]aneN₄)]²⁺, [Co([16]aneN₄)]²⁺, [Co(Bzo₂[14]aneN₄)]²⁺ and [Co(Bzo₂[16]aneN₄)]²⁺ that have also been prepared and characterized.

The C, H, N analysis results of the neat cobalt complexes showed close similarity to the theoretical values. The molecular formula of the tetraaza complexes has been assigned on the basis of the results of their elemental analyses. A preliminary identification of the metal complexes was made on the basis of their IR spectra which exhibited no bands characteristic of free primary amine, thus supporting the proposed macrocyclic skeleton (Scheme 1). The cobalt contents of the zeolite encapsulated catalysts were estimated by dissolving known amounts of the catalyst in conc. HCl and from these solutions, the cobalt contents were estimated by using AAS. The chemical compositions (Table 3) confirmed the purity and stoichiometry of the neat and encapsulated complexes. The chemical analyses of the samples revealed the presence of organic matter with an C/N ratio roughly similar to that for neat complexes. In Table 3, the mol ratios Si/Al obtained by chemical analysis for zeolites have been presented. The Si and Al contents in Co(II)–NaY and the zeolite complexes were almost in the same ratio as in the parent zeolite. This indicates little changes in the zeolite framework due to the absence of de-alumination in metal ion exchange. The parent NaY zeolite has Si/Al molar ratio of 2.53 which corresponds to a unit cell formula [Na₅₆(AlO₂)₅₆(SiO₂)₁₃₆]. The unit cell formula of metal-exchanged zeolites showed a cobalt dispersion of 11 moles per unit cell [(Na_{33.8}Co₁₁(AlO₂)₅₆(SiO₂)₁₃₆·nH₂O). Metal ion exchange at around 34% leads to 2.70–3.70% of metal loading in zeolite.

The analytical data of each complex indicated that Co:C:N molar ratio is almost close to those calculated for the mononuclear structure. However, the presence of minute traces of free [Co(N–N)₂]²⁺ in the lattice can be assumed as the [Co(N–N)₂]²⁺ content which is slightly higher than the stoichiometric requirement only a portion

of [Co(N–N)₂]²⁺ in exchanged zeolite that has undergone complexation and the rest is expected to be removed on re-exchange with NaCl solution. The X-ray diffractograms of the complex nanoparticles entrapped in the nanoreactor of zeolite-Y containing the Co(II) complexes did not reveal any significant difference from those of NaY. The encapsulation of the cobalt complexes inside the zeolite nanocavities is indicated by the absence of extraneous material and scanning electron microscopy (SEM). Both X-ray diffraction and SEM indicated that zeolites with good crystallinity can be obtained during the encapsulation of [Co([14 or 16]aneN₄)]²⁺ and [Co(Bzo₂[14 or 16]aneN₄)]²⁺ complexes by the one pot template condensation reaction.

The surface area and pore volume of the catalysts have been presented in Table 4. The encapsulation of [Co([14]aneN₄)]²⁺, [Co([16]aneN₄)]²⁺, [Co(Bzo₂[14]aneN₄)]²⁺ and [Co(Bzo₂[16]aneN₄)]²⁺ complexes in zeolite reduced the adsorption capacity and the surface area of the zeolite. The lowering of the pore volume and surface area indicated the presence of complexes within the zeolite nanocages and not on the external surface.

As shown in Table 5, the Co (2p_{3/2}) binding energy (E_b) is 781.9.7 and 780.7 eV in the [Co([14]aneN₄)](ClO₄)₂ complex and cobalt(II) chloride, respectively. The Co (2p_{3/2}) binding energy of the cobalt(II) complex has been increased 1.4 eV compared with that of the cobalt(II) chloride. The results indicate that the charge on the metals decreases when complexes were formed. The encapsulated complexes are referenced to the binding energy of 102.7 eV for the Si 2p core level due to its extensive use of this binding energy in NaY system [44,45]. However, the neat complexes are referenced to the binding energy of 292.7 eV for the K 2p_{3/2} core level. Table 5 shows the Co 2p core levels of the neat and the encapsulated complexes. Cobalt remains in the +2 oxidation states in both the neat and the encapsulated complexes and it matches well with the reported values for similar systems [45]. There is a high increase in satellite intensity for Co 2p levels and a large energy gap (~17 eV) in the encapsulated complex which shows the higher catalytic activity than the neat complex.

3.3. Catalytic activity

The epoxidation of styrene is negligible in the absence of cobalt catalysts confirming that under the conditions of the experiments,

Table 4

Surface area and pore volume data of tetraaza macrocyclic cobalt (II) complex nanoparticles entrapped in the nanoreactor of zeolite-Y.

Sample	Surface area ^a (m ² /g)	Pore volume ^b (ml/g)
NaY	545	0.31
Co(II)–NaY	532	0.30
[Co([4]aneN ₄)] ²⁺ –NaY	418	0.17
[Co([16]aneN ₄)] ²⁺ –NaY	410	0.15
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ –NaY	372	0.12
[Co(Bzo ₂ [16]aneN ₄)] ²⁺ –NaY	363	0.10

^a Surface area is the "monolayer equivalent area" calculated as explained in the reference [22,23].

^b Calculated by the *t*-method.

Table 5

XPS data of neat and nanopores of zeolite-Y tetraaza macrocyclic cobalt (II) complexes.

Sample	E_b , Co 2p _{3/2} (eV)	2p _{3/2} and 2p _{1/2} separation (eV)
[Co([14]aneN ₄)](ClO ₄) ₂	781.9	15.6
[Co([14]aneN ₄)] ²⁺ –NaY	782.8	16.3
[Co([16]aneN ₄)](ClO ₄) ₂	781.7	15.5
[Co([16]aneN ₄)] ²⁺ –NaY	782.5	16.2
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂	782.4	15.9
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ –NaY	783.0	17.0
[Co(Bzo ₂ [16]aneN ₄)](ClO ₄) ₂	782.2	15.5
[Co(Bzo ₂ [16]aneN ₄)] ²⁺ –NaY	782.4	15.8
CoCl ₂	780.7	15.3

Table 6
Epoxidation of styrene with molecular oxygen catalyzed by a variety of catalysts based on tetraaza macrocyclic cobalt (II) complexes^a.

Catalyst	Styrene conversion (%)	Epoxide selectivity (%)
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂	47.7	56.3
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂ ^b	28.6	58.9
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂ ^c	45.3	52.3
[Co(Bzo ₂ [14]aneN ₄)](ClO ₄) ₂ ^d	33.9	41.4
[Co(Bzo ₂ [16]aneN ₄)](ClO ₄) ₂	40.9	57.8
[Co([14]aneN ₄)](ClO ₄) ₂	42.6	50.2
[Co([16]aneN ₄)](ClO ₄) ₂	36.5	53.4
CoCl ₂	16.1	30.2

^a Reaction conditions: amount of cobalt(II) tetraaza macrocycle complex as catalyst: 1.30 mmol; reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 ml; reaction time, 6 h.

^b Catalyst = 0.65 mmol.

^c Catalyst = 2.60 mmol.

^d Catalyst = 3.90 mmol.

the epoxidation is indeed catalytic in nature. In the case of the encapsulated catalysts, metal was not detected in the reaction products by AAS indicating that epoxidation of styrene by dissolved metal complexes leached out from the zeolite matrix is negligible. The host alone without the cobalt complexes was also catalytically inactive. Further evidence confirms that the epoxidation of styrene is indeed catalyzed to a significant extent by the solid zeolite catalyst containing the encapsulated metal complex and not by the free complex dissolved in solution as follows: in one set of two identical experiments, the solid catalyst ([Co(Bzo₂[14]aneN₄)]²⁺-NaY) was removed by centrifugation after a reaction time of 10 h. While the conversion of styrene proceeded further in the presence of the solid catalyst, there was no further conversion of styrene when the catalyst was removed from the reaction system. The following points may be noted:

1. The tetraaza macrocyclic ligands ([14]aneN₄, [16]aneN₄, Bzo₂[14]aneN₄, Bzo₂[16]aneN₄) alone in the absence of metal were not catalytically active.
2. The zeolite-encapsulated complexes did not undergo any colour change during the reaction and could be easily separated and reused many times. In contrast, the neat complexes, while they were active in the first cycle, were completely destroyed during the first run and changed colour.

Table 7
Epoxidation of styrene with molecular oxygen catalyzed by variety of catalysts based on tetraaza macrocyclic cobalt (II) complex nanoparticles entrapped in the nanoreactor of zeolite-Y^a.

Catalyst	Solvent	Temperature (K)	Styrene conversion (%)	Epoxide selectivity (%)
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMF	373	42.1	86.6
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY ^b	DMF	373	41.5	84.7
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY ^c	DMF	373	40.3	83.1
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY ^d	DMF	373	39.6	82.8
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMF	363	30.9	75.3
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMF	353	21.4	64.1
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMF	343	12.0	50.3
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMA	373	44.2	87.5
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	DMSO	373	24.7	2.6
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	Py	373	-	-
[Co(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	Monochlorobenzene	373	-	-
[Co(Bzo ₂ [16]aneN ₄)] ²⁺ -NaY	DMF	373	34.6	89.4
[Co([14]aneN ₄)] ²⁺ -NaY	DMF	373	38.7	76.4
[Co([16]aneN ₄)] ²⁺ -NaY	DMF	373	31.2	80.7
Co(II)-NaY	DMF	373	48.2	60.1

DMF: *N,N*-dimethylformamide. DMA: *N,N*-dimethylacetamide. DMSO: dimethyl sulfoxide.

^a Reaction conditions: the amount of transition metal ions in catalysts was fixed at 1.30 mmol; styrene, 10 mmol; DMF, 20 ml; reaction time, 6 h.

^b First reuse

^c Second reuse

^d Third reuse.

3. At the end of reaction, the catalyst was separated by filtrations, thoroughly washed with solvent and reused under similar conditions by AAS which showed no reduction in the amount of metal.
4. Conversion for cobalt(II) complexes with different macrocyclic ligands decreased in the order: Bzo₂[14]aneN₄ > [14]aneN₄ > Bzo₂[16]aneN₄ > [16]aneN₄ (for "neat" and encapsulated complexes) (Tables 6 and 7). Meanwhile, Co(II)-NaY is active catalyst in styrene conversion similar to neat and encapsulated complexes, but it has low epoxide selectivity than others.
5. One of the major drawbacks of homogeneous metal complexes as catalysts is their irreversible deactivation due to formation of μ -oxo and μ -peroxo dimeric and other polymeric species especially when they were used as oxidant. This problem may be avoided by isolating the metal tetraaza macrocyclic complexes from each other by encapsulation in the nanopores of a molecular sieve. The stability increases by several orders of magnitude when the cobalt(II) complexes were isolated from each other by encapsulation within the nanocavity of the faujasite zeolites (Scheme 2). Since the formation of these bulky dimeric and polymeric species is sterically impossible when the monomeric complex was encapsulated and physically confined within the nanopores of zeolite, it is anticipated that the encapsulated catalysts would be more rugged and can be recycled for using. The data in Table 7 supports the above hypothesis.
6. The catalytic oxidation of styrene was studied with complex nanoparticles entrapped in the nanoreactor of zeolite-Y using O₂ as the oxidant. The blank reactions performed over NaY zeolite under identical conditions showed only negligible conversion indicating that zeolite host is inactive for oxidation (Table 7). Furthermore, O₂ alone is unable to oxidize the substrates in the absence of any catalyst. In representative tests, zeolite complex was filtered out and the filtrate was analyzed for metal content using atomic absorption spectrophotometry. The absence of metal ions in solution phase indicates that no leaching of complexes occurs during reaction when they are too intact in the pores. These observations suggest that the oxidations occur due to the catalytic nature of the encapsulated tetraaza macrocyclic complexes and no playing significant role by either the zeolite support or free complexes.
7. Transition metal complex-based soluble catalysts are more prone to deactivation by the dimerization of active centers

Table 8
Epoxidation of styrene with various oxidants over the $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)]^{2+}-\text{NaY}$ (Co, 1.30 mmol)^a.

Oxidant	Styrene conversion (%)	Epoxide selectivity (%)
None ^b	–	–
O ₂	42.1	86.6
H ₂ O ₂	35.4	80.1
TBHP	49.6	28.6
NaClO	2.8	90.7

^a Reaction conditions: reaction temperature, 373 K; styrene, 10 mmol; DMF, 20 ml; reaction time, 6 h.

^b The reaction was carried out under nitrogen atmosphere without adding an oxidant.

which is expected to be reduced by encapsulating them in zeolites. Host-guest nanocatalysts were recycled for the epoxidation of styrene with molecular oxygen with a view to establish the effect of encapsulation on stability. The initial run has shown a conversion of 42.1% and it is only marginally reduced to 41.5% on recycling the catalyst. The results indicate that the complex nanoparticles entrapped in the nanoreactor of zeolite-Y are almost stable to be recycled and used for the oxidation of styrene without much loss in activity. Thus, the encapsulation of complexes in nanopores of zeolites increases the life of the catalyst by reducing dimerization due to the restriction of internal framework structure. IR spectrum of the recycled sample is quite similar to the fresh sample and indicates little changes in the coordination of tetraaza macrocyclic after the oxidation reactions.

- After the reaction, the liquid filtrate was subjected to atomic absorption spectroscopic analysis and no amount of cobalt could be detected. When the liquid filtrate was used in the reaction instead of the solid catalyst, no significant conversion of styrene was observed. Moreover, CoCl_2 or $[\text{Co}(\text{[14]aneN}_4)](\text{ClO}_4)_2$, $[\text{Co}(\text{Bzo}_2[16]\text{aneN}_4)](\text{ClO}_4)_2$, $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)](\text{ClO}_4)_2$ and $[\text{Co}(\text{[16]aneN}_4)](\text{ClO}_4)_2$ are homogeneous catalysts similar to heterogeneous catalysts in styrene conversion but, heterogeneous catalysts is highly effective than homogeneous catalysts in epoxide selectivity, as shown in Tables 6 and 7. It is supposed that the epoxidation proceeds heterogeneously over the $[\text{Co}(\text{[14 or 16]aneN}_4)]^{2+}$, $[\text{Co}(\text{[14 or 16]aneN}_4)]^{2+}$ -faujasite zeolite. On the other hand, the leaching of active component (redox center) from molecular sieve-based catalysts seems to be a serious problem when hydrogen peroxide or organic hydroperoxide is used as the oxidant for epoxidation. It is probably true because hydrogen peroxide or organic hydroperoxide has a marked ability to dissolve the redox component from molecular sieves into the liquid phase [46]. Therefore, the use of molecular oxygen as the oxidant in this system also has advantages including increasing the stability against leaching for zeolite based heterogeneous catalysts and thus may provide another opportunity to exploit the redox molecular sieves for liquid phase-selective oxidation reactions.
- Table 7 shows the effect of reaction temperature on the catalytic performances of the $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)]^{2+}-\text{NaY}$. At temperature lower than 363 K, not only styrene conversion but also styrene oxide selectivity decreased remarkably with the reaction temperature (Table 7). The selectivity for styrene oxide and benzaldehyde remained almost unchanged with the reaction time, indicating that benzaldehyde might mainly be formed in parallel with styrene oxide.
- Various solvents with relatively low volatility (b.p. > 373 K) have been tested for the epoxidation of styrene by molecular oxygen over the $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)]^{2+}-\text{NaY}$ catalyst. The results have been summarized in Table 7. As shown in Table 7, the solvents played a crucial role in the epoxidation reactions. It is significant to note that the acylamides including dimethylformamide (DMF) and dimethylacetamide (DMA) are particularly efficient in providing both high styrene conversion and high epoxide selectivity. Although high styrene conversion could be obtained when dimethyl sulfoxide (DMSO) was used, the selectivity for styrene oxide was low. No reaction occurred when nitrogen- or chloro-containing solvents such as pyridine and monochlorobenzene were used. It should be noted that *tert*butyl alcohol, a potential co-reductant for the activation of molecular oxygen [47], did not work here. The use of DMF (or DMA) as the solvent may suggest several possible roles such as coordination with cobalt sites to form the true active sites during the reaction and/or acting as a co-reductant.
- Table 8 shows the catalytic performances for the epoxidation of styrene with different oxidants over the $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)]^{2+}-\text{NaY}$ catalyst. No styrene conversion was observed when the reaction was carried out under Ar or a pure N₂ atmosphere without any oxidants. In the case of molecular oxygen over catalyst, styrene oxide and benzaldehyde were produced. Very low activity was obtained with NaClO over catalyst. Although styrene conversion was high with TBHP, styrene oxide selectivity was very low over catalyst. In addition to benzaldehyde (40%), polymeric products were probably among the by-products in the case of TBHP, indicating the occurrence of uncontrollable free radical reactions. Hydrogen peroxide gave reasonably good performance for the epoxidation of styrene but styrene conversion was lower compared with that observed by molecular oxygen over catalyst. The rapid decomposition of hydrogen peroxide into molecular oxygen over the catalyst at the initial stage would be the main reason for the lower activity. Therefore, the current co-based catalysts are very specific in the activation of molecular oxygen for the epoxidation of alkenes.
- It is well known that many cobalt(II) complexes can bind and activate molecular oxygen to form complexes comprising cobalt(III)-(O²⁻) [48]. It is supposed that in this research work system, a similar binding of molecular oxygen to the cobalt(II) sites located in the molecular sieves may also occur in the initial step. The formed Co(III)-(O²⁻) species might undergo further reactions to generate an active oxygen species with a radical nature which is responsible for the epoxidation. It is known that cobalt(III) ions may catalyze the formation of an acylperoxy radical from benzaldehyde by molecular oxygen [49]. The acylperoxy radical may epoxidize alkenes to give epoxides and benzoic acid. In this research work system, although benzaldehyde was formed as a main by-product, it was not observed the formation of a significant amount of benzoic acid. Moreover, the epoxidation was not significantly enhanced when an excess of benzaldehyde was added to the reactant mixture. Therefore, it can be excluded the possibility that benzaldehyde may act as the co-reductant. However, DMF itself may act as a co-reductant in the formation of active oxygen species. To clarify this point, the influence of the addition of a radical scavenger, butyl hydroxy toluene on catalytic performances has been investigated. The results revealed that over $[\text{Co}(\text{Bzo}_2[14]\text{aneN}_4)]^{2+}-\text{NaY}$ catalyst styrene conversion decreased to almost zero after the addition of a small amount of butyl hydroxy toluene under the reaction conditions. This observation confirms the radical nature of the active oxygen species formed by the activation of molecular oxygen over the cobalt(II) site.
- The activity of styrene oxidation decreases in the series $[\text{Co}(\text{tetraaza})](\text{ClO}_4)_2 > \text{CoCl}_2$. The trend observed in Tables 6 and 7 can be explained by the donor ability of ligand available in the complex catalysts. As Wang and co-workers

have pointed out recently, the key point in the conversion of olefin to the products is the reduction of $L-Co^{3+}$ to $L-Co^{2+}$. This reduction to $L-Co^{2+}$ is facilitated with the ligands available around the metal cation [50]. As mentioned before [51–56], higher activity of $[Co(BzO_2[14]aneN_4)]^{2+}-NaY$ complex might be attributed to the higher activity of aromatic ligand and its more active cation radical intermediate with respect to the aliphatic ligand system ethylene or propylene diamine. Lower activity of $[Co([16]aneN_4)]^{2+}-NaY$ can be accounted by the substantial steric hindrance of propylene groups that prevents the approaching oxidant toward the central metal of the catalyst.

4. Conclusion

The cobalt(II) tetraaza macrocycle encapsulated in nanopores of zeolite-Y can catalyze the epoxidation of styrene by molecular oxygen almost the same to cobalt(II) tetraaza macrocycle but, epoxide selectivity is higher efficiency in the liquid phase. Oxygen is found to be the best oxidant for epoxidation reactions than H_2O_2 , TBHP, and $NaClO$ over $[Co(BzO_2[14]aneN_4)]^{2+}-NaY$. Oxygen species with a produced radical nature via the activation of molecular oxygen have been proposed for the epoxidation reactions. These catalyst systems offer structural integrity by having a uniform distribution of the cobalt complex in the nanopore structure of the support. The zeolite framework keeps the guest complexes and prevents their dimerization leading to the retention of catalytic activity. The encapsulated complexes exhibit enhanced stability and selectivity in the oxidation reactions. These encapsulated systems offer structural integrity by having a uniform distribution of the metal complex in the pore structure of the support. Future work on this system is expected to envisage its industrial applications for partial oxidation reactions.

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