

Host (nanocavity of zeolite-Y)/guest (12- and 14-membered azamacrocyclic Ni(II) complexes) nanocatalyst: synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen

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Abstract Ni(II) complexes of [12]aneN₄: 1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone; [14]aneN₄: 1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone; Bzo₂[12]aneN₄: dibenzo-1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone and Bzo₂[14]aneN₄: dibenzo-1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone have been encapsulated in the nanopores of zeolite-Y by a two-step process in the liquid phase: (i) adsorption of [bis(diamine)nickel(II)]; [Ni(N–N)₂–NaY; in the supercages of the zeolite, and (ii) in situ condensation of the nickel(II) precursor complex with diethyloxalate. The new host-guest nanocatalyst (HGN) were characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV/Vis, XRD, BET, DRS) and then were used for oxidation of cyclohexene with molecular oxygen.

Keywords Nanocatalyst · Nickel(II) · Azamacrocyclic · Nanopores · Oxidation

Introduction

Nanotechnology has gained substantial popularity recently due to the rapidly developing techniques both to synthesize and characterize materials and devices at the nanoscale, as well as the promises that such technology offers to substantially expand the achievable limits in many different fields including medicine, electronics, chemistry, and engineering. In the literature, there are constantly reports of new discoveries of unusual phenomena due to the small scale and new applications. Nanosize metal particles have occupied a central place in heterogeneous catalysis for many years, long before recognition of nanotechnology. Thus, it is fitting to critically evaluate the impact of such development on heterogeneous catalysis [1, 2].

The term nanoporous materials have been used for those porous materials with pore diameters of less than 100 nm. Many kinds of crystalline and amorphous nanoporous materials such as framework silicates and metal oxides, zeolites, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons have been described lately in the literature [3]. Nanoporous materials are exemplified by crystalline framework solids such as zeolites, whose crystal structure defines channels and cages, i.e., nanopores, of strictly regular dimensions. They can impart shape selectivity for both the reactants and products when involved in the chemical reactions and processes. The large internal surface area and void volumes with extremely narrow pore size distribution as well as functional centers homogeneously dispersed over the surface make nanoporous solids highly active materials. Over the last decade, there has been a dramatic increase in synthesis, characterization and application of novel nanoporous materials [4–9].

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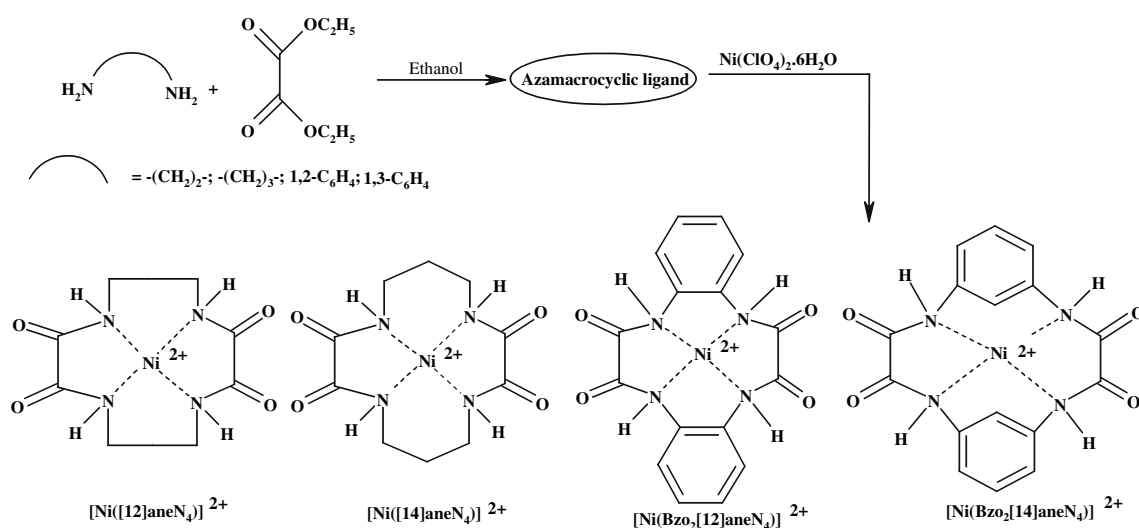
In this work were chosen the tetraaza–tetraone ligands and their encapsulated complexes (Schemes 1, 2) in the oxidation reaction. Because, so far, have not been used encapsulated tetraaza–tetraone nickel complexes within the zeolite-Y in the oxidation of cyclohexene. The use of these encapsulated complexes as nanocatalysts can enhance and increase the catalytic activity in the oxidation reaction. The encapsulated complexes can be as windows to the selection a suitable nanocatalyst for the oxidation reaction. In this paper, we report the synthesis and characterization of nickel(II) complexes of 12- and 14-membered tetraaza macrocyclic ligand; [12]aneN₄: 1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone; [14]aneN₄: 1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone; Bzo₂[12]aneN₄: dibenzo-1,4,7,10-tetraazacyclododecane-2,3,8,9-tetraone and Bzo₂[14]aneN₄: dibenzo-1,4,8,11-tetraazacyclotetradecane-2,3,9,10-tetraone; encapsulated within the nanopores of zeolite-Y by the template condensation of diethyloxalate and [bis(diamine) nickel(II)]; [Ni([12]aneN₄)]²⁺–NaY, [Ni([14]aneN₄)]²⁺–NaY; [Ni(Bzo₂[12]aneN₄)]²⁺–NaY; [Ni(Bzo₂[14]aneN₄)]²⁺–NaY; shown in Schemes 1, 2 and used in the oxidation of cyclohexene with molecular oxygen.

Experimental

Materials and physical measurements

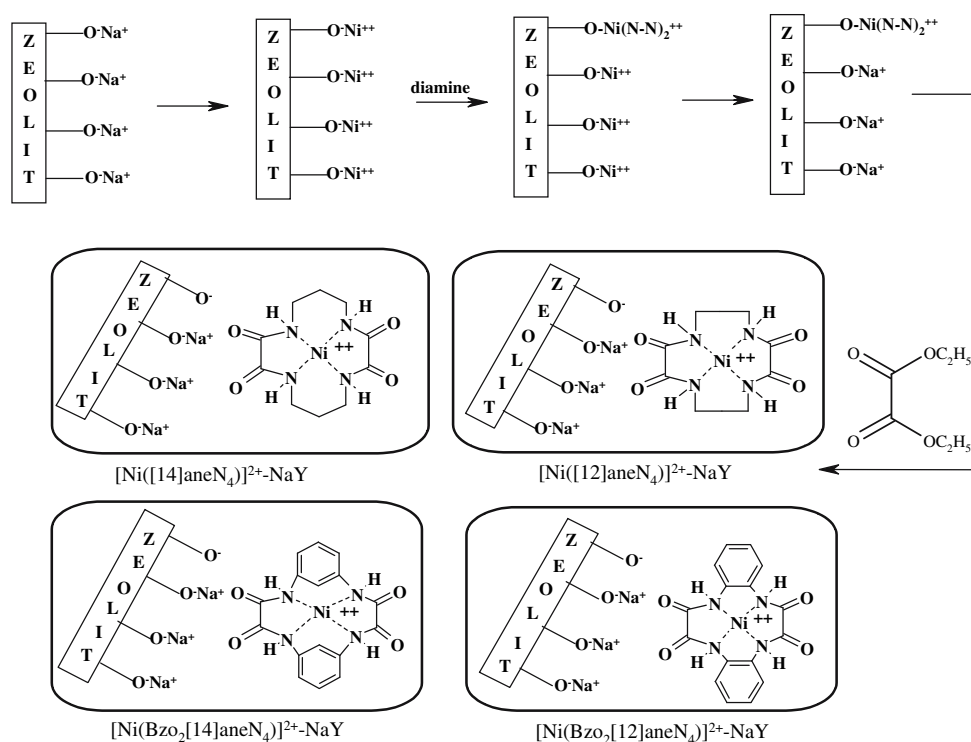
Cyclohexene was distilled under nitrogen and stored over molecular sieves (4 Å). Cyclohexanone was used as an internal standard for the quantitative analysis of the product using gas chromatography. Reference samples of

2-cyclohexene-1-ol and 2-cyclohexene-1-one (Aldrich) were distilled and stored in the refrigerator. NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). 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 after the synthesis of the catalysts as determined by UV–Vis spectroscopy, from the amount taken for the synthesis. Atomic absorption spectra (AAS) were recorded on a Perkin-Elmer 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 1,500–200 nm, using MgO as reference. 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 diffractometer 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 [10].



Scheme 1

Scheme 2



Synthesis of azamacrocyclic ligand

Azamacrocyclic ligand ([12]aneN₄, [14]aneN₄, Bzo₂[12]aneN₄ and Bzo₂[14]aneN₄) was prepared by following the procedures reported in Ref. [11]. The hot ethanolic solution (20 cm³), of diethyloxalate (2.9228 g, 0.02 mol), and a hot ethanolic solution (20 cm³) of diamine (0.02 mol); 1,2-diaminoethane (1.20 g), 1,3-diaminopropane (1.48 g), 1,2-diaminobenzene (2.16 g), 1,3-diaminobenzene (2.16 g) were mixed slowly with constant stirring. This mixture was refluxed for 7 h in the presence of few drops of concentrated HCl. On cooling a solid precipitate was formed, which was filtered, washed with cold EtOH, and dried under vacuum over P₄O₁₀. Anal. Calcd for [12]aneN₄: C, 42.11; H, 5.30; N, 24.54; C/N, 1.72. Found: C, 41.92; H, 5.18; N, 24.66; C/N, 1.70; $\nu_{\text{N-H}}$, 3314 cm⁻¹; $\nu_{\text{C=O}}$, 1,663 cm⁻¹. Anal. Calcd for [14]aneN₄: C, 46.87; H, 6.29; N, 21.85; C/N, 2.14. Found: C, 46.67; H, 6.13; N, 21.99; C/N, 2.12; $\nu_{\text{N-H}}$, 3398 cm⁻¹; $\nu_{\text{C=O}}$, 1,651 cm⁻¹. Anal. Calcd for Bzo₂[12]aneN₄: C, 59.26; H, 3.73; N, 17.27; C/N, 3.43. Found: C, 59.04; H, 3.52; N, 17.39; C/N, 3.40; $\nu_{\text{N-H}}$, 3325 cm⁻¹; $\nu_{\text{C=O}}$, 1,678 cm⁻¹. Anal. Calcd for Bzo₂[14]aneN₄: C, 59.26; H, 3.73; N, 17.27; C/N, 3.43. Found: C, 59.00; H, 3.48; N, 17.41; C/N, 3.39; $\nu_{\text{N-H}}$, 3,318 cm⁻¹; $\nu_{\text{C=O}}$, 1,675 cm⁻¹.

Synthesis of [Ni(azamac.)](ClO₄)₂

For preparation of “neat” complexes: nickel(II) perchlorate hexahydrate (3.66 g, 0.01 mol) was dissolved in

ethanol (20 mL) was reacted with an ethanolic (20 mL) solution of azamacrocyclic ligands ([12]aneN₄, [14]aneN₄, Bzo₂[12]aneN₄ or Bzo₂[14]aneN₄) (0.01 mol) by refluxing for 1 h under nitrogen atmosphere. The mixture was heated at reflux for 6 h until a yellow solution resulted. The solution was cooled to room temperature and filtered to remove nickel hydroxide. Excess lithium perchlorate dissolved in methanol was added to the filtrate, and the mixture was kept in the refrigerator until yellow solid was formed. The solids were filtered, washed thoroughly with cold ethanol and dried in vacuum. Anal. Calcd for [Ni([12]aneN₄)](ClO₄)₂: C, 19.77; H, 2.47; N, 11.53; C/N, 1.71; Ni, 12.09. Found: C, 19.50; H, 2.30; N, 11.66; C/N, 1.67; Ni, 11.89%; Yield: ~57%; $\nu_{\text{N-H}}$, 3,308 cm⁻¹; $\nu_{\text{C=O}}$, 1,659 cm⁻¹; Λ , 250 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$; $d \leftrightarrow d$, 448 nm. Anal. Calcd for [Ni([14]aneN₄)](ClO₄)₂: C, 23.36; H, 3.12; N, 10.90; C/N, 2.14; Ni, 11.43. Found: C, 23.20; H, 3.01; N, 11.06; C/N, 2.10; Ni, 11.29%; Yield: ~52%; $\nu_{\text{N-H}}$, 32.94 cm⁻¹; $\nu_{\text{C=O}}$, 1,646 cm⁻¹; Λ , 245 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$; $d \leftrightarrow d$, 463 nm. Anal. Calcd for [Ni(Bzo₂[12]aneN₄)](ClO₄)₂: C, 33.01; H, 2.66; N, 9.63; C/N, 3.43; Ni, 10.09. Found: C, 32.89; H, 2.50; N, 9.80; C/N, 3.36; Ni, 9.91%; Yield: ~46%; $\nu_{\text{N-H}}$, 3,318 cm⁻¹; $\nu_{\text{C=O}}$, 1,672 cm⁻¹; $d \leftrightarrow d$, 441 nm. Anal. Calcd for [Ni(Bzo₂[14]aneN₄)](ClO₄)₂: C, 33.01; H, 2.66; N, 9.63; C/N, 3.43; Ni, 10.09. Found: C, 32.89; H, 2.50; N, 9.80; C/N, 3.36; Ni, 9.91%; Yield: ~46%; $\nu_{\text{N-H}}$, 3,318 cm⁻¹; $\nu_{\text{C=O}}$, 1,672 cm⁻¹; Λ , 242 $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$; $d \leftrightarrow d$, 441 nm. Anal. Calcd for [Ni(Bzo₂[14]aneN₄)](ClO₄)₂: C, 33.01; H, 2.66; N, 9.63; C/N, 3.43; Ni, 10.09. Found: C, 32.86; H, 2.52; N, 9.78; C/N,

3.36; Ni, 9.88%; Yield: ~41%; $\nu_{\text{N-H}}$, 3,313 cm^{-1} ; $\nu_{\text{C=O}}$, 1,668 cm^{-1} ; Λ , 240 $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$; $d \leftrightarrow d$, 459 nm.

Preparation of HGN; $[\text{Ni}(\text{azamac.})]^{2+}\text{-NaY}$

To prepare of Host-Guest Nanocatalyst (HGN); typically a 2 g NaY zeolite was suspended in 100 mL distilled water, which contained nickel(II) nitrate (0.025 M). The mixture was then heated while stirring at 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from any nickel(II) ion (by AAS of filtrate) content and dried for 10 h at 80 °C under vacuum. The ionic exchange degree was determined by atomic absorption spectrophotometer. To a stirred methanol solution of Ni(II)-NaY (4 g) were added 0.37 g of diamine (1,2-diaminoethane, 1,3-diaminopropane, 1,2-diaminobenzene or 1,3-diaminobenzene) suspended in 100 mL of methanol and then refluxed for 8 h under N_2 atmosphere. The light blue solid consisting of $[\text{Ni}(\text{N-N})_2]^{2+}$ denoted as $[\text{Ni}(\text{N-N})_2]^{2+}\text{-NaY}$ was collected by filtration, washed with ethanol. The resulted zeolites, were Soxhlet extracted with *N,N'*-dimethylformamide (for 4 h) and then with ethanol (for 3 h) to remove excess unreacted diamine and any Ni(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting light blue solids were dried at 60 °C under vacuum for 24 h. To a stirred methanol suspension (100 mL) of $[\text{Ni}(\text{N-N})_2]^{2+}\text{-NaY}$ (2 g) was slowly added diethylxalate (under N_2 atmosphere). The mixture was heated under reflux condition for 24 h until a pale yellow suspension resulted. The solution was filtered and the resulting zeolites, were Soxhlet extracted with *N,N'*-dimethylformamide (for 6 h) and then with ethanol (for 5 h) to remove excess unreacted products from amine-ester condensation and any nickel(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting pale yellow solids were dried at 70 °C under vacuum for 12 h. The remaining [bis(diamine)nickel(II)] ions in zeolite were removed by exchanging with aqueous 0.1 M NaNO_3 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 nickel(II) complexes encapsulated in zeolite matrix were determined by the elemental analysis and subtracting the amount of Ni(II) complex left in the solutions after the synthesis of the catalysts as determined by UV-Vis spectroscopy, from the amount taken for the synthesis. Anal. Found for NaY: Si, 21.76; Al, 8.60; Na, 7.50; Si/Al, 2.53%. Anal. Found for Ni(II)-NaY: Si, 21.79; Al, 8.62; Na, 3.28; Ni, 3.72; Si/Al, 2.53%. Anal. Found for $[\text{Ni}([12]\text{janeN}_4)]^{2+}\text{-NaY}$: C, 3.77; H, 1.41; N, 2.53; C/N, 1.49; Ni, 2.67; Si, 21.16; Al, 8.36; Na, 5.37; Si/Al, 2.53%;

$\nu_{\text{N-H}}$, 3,306 cm^{-1} ; $\nu_{\text{C=O}}$, 1,657 cm^{-1} ; $d \leftrightarrow d$, 453 nm. Anal. Found for $[\text{Ni}([14]\text{janeN}_4)]^{2+}\text{-NaY}$: C, 3.79; H, 1.43; N, 1.94; C/N, 1.95; Ni, 2.65; Si, 21.14; Al, 8.35; Na, 5.35; Si/Al, 2.53%; $\nu_{\text{N-H}}$, 3,292 cm^{-1} ; $\nu_{\text{C=O}}$, 1,641 cm^{-1} ; $d \leftrightarrow d$, 466 nm. Anal. Found for $[\text{Ni}(\text{Bzo}_2[12]\text{janeN}_4)]^{2+}\text{-NaY}$: C, 4.14; H, 1.37; N, 1.29; C/N, 3.20; Ni, 2.62; Si, 21.07; Al, 8.33; Na, 5.31; Si/Al, 2.53%; $\nu_{\text{N-H}}$, 3,311 cm^{-1} ; $\nu_{\text{C=O}}$, 1,665 cm^{-1} ; $d \leftrightarrow d$, 445 nm. Anal. Found for $[\text{Ni}(\text{Bzo}_2[14]\text{janeN}_4)]^{2+}\text{-NaY}$: C, 4.13; H, 1.38; N, 1.30; C/N, 3.17; Ni, 2.60; Si, 21.05; Al, 8.32; Na, 5.32; Si/Al, 2.53%; $\nu_{\text{N-H}}$, 3,312 cm^{-1} ; $\nu_{\text{C=O}}$, 1,660 cm^{-1} ; $d \leftrightarrow d$, 464 nm.

Oxidation of cyclohexene, general procedure

General procedure for oxidation of cyclohexene with molecular oxygen: 10 mL of cyclohexene and 1.2×10^{-5} mol of heterogeneous catalyst were added to a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle. The mixture was heated to 70 °C in water bath and stirred with a magnetic stirring bar. The oxidation reactions were performed under atmospheric pressure of molecular oxygen in the absence of solvent, and then 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the major products were resulted.

Results and discussion

The chemical compositions were confirmed the purity and stoichiometry of the neat and nanopores of zeolite-Y encapsulated complexes. The chemical analyses of the samples reveal the presence of organic matter with a C/N ratio roughly similar to for neat complexes. The Si and Al contents in Ni(II)-NaY and the zeolite complexes are almost in the same ratio as in the parent zeolite. This indicates little changes in the zeolite framework due to the absence of dealumination in metal ion exchange. The X-ray diffraction patterns of zeolite contained tetraaza complexes are similar to both the Ni(II)-NaY and the parent NaY zeolite. The zeolite crystallinity is retained on encapsulating complexes. Crystalline phase of free metal ions or encapsulation ligand complexes were not detected in any of the patterns as their fine dispersion in zeolite might have rendered them non-detectable by XRD.

The flexible ligand synthesis (Scheme 1) lead to the encapsulation of Ni(II) complexes of tetraaza tetraone ligand inside the zeolite nanopore. The parent NaY zeolite has Si/Al molar ratio of 2.53 which corresponds to a unit cell formula $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]$. The unit cell formula of metal exchanged zeolites shows a nickel dispersion of 11.2 moles per unit cell ($\text{Na}_{34.4}\text{Ni}_{11.2}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}].n\text{H}_2\text{O}$). The analytical data of each complex

indicates Ni:C:N molar ratios almost close to those calculated for the mononuclear structure. Chemical composition confirmed the formation and purity of the complexes. It is estimated from the elemental analysis that the complex molecules occupy one in every four supercages of zeolite-Y.

The “neat” complexes in acetonitrile showed a characteristic UV band of ligand origin in the region 260–300 nm. A weak band due to nickel-centered $d \leftrightarrow d$ transitions was observed in the visible range at ~ 445 nm. The size of the macrocyclic ligand affected the structure. As a consequence of this, the $d \leftrightarrow d$ band shifted from 448 nm in $[\text{Ni}([\text{12}] \text{aneN}_4)](\text{ClO}_4)_2$ to 463 nm in $[\text{Ni}([\text{14}] \text{aneN}_4)](\text{ClO}_4)_2$. The ligand-centered band also shifted from 281 nm in $[\text{Ni}([\text{12}] \text{aneN}_4)](\text{ClO}_4)_2$ to 264 nm in $[\text{Ni}([\text{14}] \text{aneN}_4)](\text{ClO}_4)_2$. This shift in the band position to higher energy side indicates that the 12-membered tetraaza tetraone ligands provides higher stability than the 14-membered tetraaza tetraone ligands and the ligand field is stronger in 12-membered than in 14-membered complexes. When the complexes were encapsulated in zeolite-Y, the $d \leftrightarrow d$ band shifted again to the higher energy side (by 5 nm in $[\text{12}] \text{aneN}_4$ and 4 nm in $\text{Bzo}_2[\text{12}] \text{aneN}_4$ complexes). The stability of the complexes increases apparently when they are encapsulated in zeolite-Y. The position of the $d \leftrightarrow d$ band corresponds to a square-planar geometry for azamacrocyclic nickel(II) complexes [12].

The molar conductance values of tetraaza macrocyclic complexes ($\sim 240 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$) and measured correspond to 1:2 electrolytes. IR spectrum of the ligands does not exhibit any band corresponding for the free primary diamine and ketonic group. Four new bands, were appeared in the spectrum of ligand [13] in the regions 1651, 1518, 1226 and 762 cm^{-1} that are assignable 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 $[\varphi(\text{C}=\text{O})]$ bands, respectively. These evidence support the macrocyclic nature of the ligand. A single sharp band observed at $3,300 \text{ cm}^{-1}$, may be due to $\nu(\text{N}-\text{H})$ of the secondary amino group [14]. On complexation the position of $\nu(\text{N}-\text{H})$ bands shifted to lower frequency compared to the macrocyclic ligand and a new medium intensity band appeared at $\sim 470 \text{ cm}^{-1}$ attribute to $\nu(\text{Ni}-\text{N})$, it provide, strong evidence for the involvement of nitrogen in coordination. IR spectrum indicates that the ligand acts as tetradentate coordinating through nitrogen $[\text{N}_4]$. The IR bands of all encapsulated complexes were weak due to their low concentration in the zeolite. Ni(II) complexes encapsulated in the zeolite cages did not show any significant shift in N–H or C=O stretching modes. We did not notice any appreciable changes in the frequencies of Ni(II) complexes after incorporation into zeolite matrix.

The X-ray diffractograms of the catalysts containing the Ni(II) complexes did not reveal any significant difference

from those of NaY. The encapsulation of the nickel complexes inside the zeolite cavities is indicated by the absence of extraneous material by scanning electron microscopy (SEM). Both XRD and SEM indicated that zeolites with good crystallinity can be obtained during the encapsulation of $[\text{Ni}(\text{azamac.})]^{2+}$ complexes by the one pot template condensation reaction.

The surface area and pore volume of the catalysts are shown in Table 1. The inclusion of Ni(II) azamacrocyclic complexes dramatically reduces the adsorption capacity and the surface area of the zeolite. It has been reported [15] that the BET surface area of X and Y zeolite containing phthalocyanine complexes are typically less than $100 \text{ m}^2 \text{ g}^{-1}$. The lowering of the pore volume and surface area indicate the presence of azamacrocyclic nickel(II) complexes within the cavities of the zeolites and not on the external surface.

The azamacrocyclic nickel(II) complexes exhibited good activity in the oxidation of cyclohexene using molecular oxygen (Table 2). Blank reactions performed over NaY zeolite under identical conditions show only negligible conversion indicating that zeolite host is inactive for oxidation. Furthermore, O_2 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 nickel content using atomic absorption spectrophotometry. The absence of metal ions in solution phase indicates that no leaching of complexes has occurred during reaction, as they are too intact in the pores. These observations suggest that the oxidations occur due to the catalytic nature of the encapsulated azamacrocyclic complexes and no significant role is played by either the zeolite support or free complexes.

2-Cyclohexene-1-ol is the major product and 2-cyclohexene-1-one are also formed in small quantities (Table 2). The type of the azamacrocyclic ring and encapsulation affected the activity and product selectivity. Conversion for nickel(II) complexes with different azamacrocyclic ligands

Table 1 Surface area and pore volume data of azamacrocyclic Ni(II) complexes encapsulated in nanopores of zeolite Y

Sample	Surface area ^a (m^2/g)	Pore volume ^b (mL/g)
NaY	545	0.31
Ni(II)–NaY	528	0.31
$[\text{Ni}([\text{12}] \text{aneN}_4)]^{2+}$ –NaY	500	0.30
$[\text{Ni}([\text{14}] \text{aneN}_4)]^{2+}$ –NaY	495	0.26
$[\text{Ni}(\text{Bzo}_2[\text{12}] \text{aneN}_4)]^{2+}$ –NaY	478	0.23
$[\text{Ni}(\text{Bzo}_2[\text{14}] \text{aneN}_4)]^{2+}$ –NaY	470	0.22

^a Surface area is the “monolayer equivalent area” calculated as explained in the Reference 17

^b Calculated by the *t*-method

Table 2 Oxidation of cyclohexene with molecular oxygen catalyzed by “neat” azamacrocyclic nickel(II) complexes (reaction condition: 1 atm of O₂; time 8 h; catalyst 1.2×10^{-5} mol; substrate, cyclohexene 10 mL, temperature (70 °C))

Catalyst	Conversion (%)	Selectivity (%)	
		2-Cyclohexene-1-ol	2-Cyclohexene-1-one
[Ni([12]aneN ₄)(ClO ₄) ₂]	56.4	61.4	38.6
[Ni([14]aneN ₄)(ClO ₄) ₂]	52.8	63.9	36.1
[Ni(Bzo ₂ [12]aneN ₄)(ClO ₄) ₂]	65.5	68.5	31.5
[Ni(Bzo ₂ [12]aneN ₄)(ClO ₄) ₂] ^a	46.5	73.9	26.1
[Ni(Bzo ₂ [12]aneN ₄)(ClO ₄) ₂] ^b	59.3	67.7	32.3
[Ni(Bzo ₂ [12]aneN ₄)(ClO ₄) ₂] ^c	40.9	67.4	32.6
[Ni(Bzo ₂ [14]aneN ₄)(ClO ₄) ₂]	55.3	69.7	30.3

^a Catalyst = 0.5×10^{-5} mol^b Catalyst = 2.04×10^{-5} mol^c Catalyst = 4.08×10^{-5} mol

decreased in the order: Bzo₂[12]aneN₄ > [12]aneN₄ > Bzo₂[14]aneN₄ > [14]aneN₄ (for “neat” and encapsulated complexes) (Tables 2 and 3). The encapsulated complexes exhibited higher activity than the “neat” complexes.

As mentioned before [9], higher activity of [Ni(Bzo₂[12]aneN₄)]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 ethylenediamine with the conversion percentage of 61.8%. Lower activity of [Ni([14]aneN₄)]²⁺-NaY can be accounted for by the substantial steric hindrance of propylene groups that prevent the approaching oxidant toward the central metal of the catalyst.

Homogeneous catalysts are more prone to deactivation by the dimerization of active centers, which is expected to be reduced by encapsulating them in zeolites. [Ni(Bzo₂[12]aneN₄)]²⁺-NaY was recycled for the oxidation of cyclohexene with molecular oxygen with a view to establish the effect of encapsulation on stability. The initial run has showed a conversion of 70.1% and it is only marginally

reduced to 69.8% on recycling the catalyst. These results indicate that [Ni(Bzo₂[14]aneN₄)]²⁺-NaY complex is almost stable to be recycled for the oxidation of cyclohexene without much loss in activity. Thus, the encapsulation of complexes in zeolites is found to increase 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 that of fresh sample indicating little changes in the coordination of Bzo₂[12]aneN₄ after the oxidation reactions.

The results clearly suggest that [Ni(Bzo₂[12]aneN₄)]²⁺-NaY efficiently catalyses conversion of cyclohexene to 2-cyclohexene-1-ol with 71.9% selectivity. More activity of Bzo₂[12]aneN₄ system has clearly arisen from the existence of electron donating ligand which facilitate the electron transfer rate, a process that has previously observed by us in other oxidation reactions [16]. All conversions efficiency with high selectivity obtained in this study is significantly higher than that obtained using metal containing porous and nonporous materials [17].

Table 3 Oxidation of cyclohexene with molecular oxygen catalyzed by HGN (reaction condition: 1 atm of O₂; time 8 h; catalyst 1.2×10^{-5} mol; substrate, cyclohexene 10 mL)

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)	
			2-Cyclohexene-1-ol	2-Cyclohexene-1-one
[Ni([12]aneN ₄)] ²⁺ -NaY	70	61.8	63.4	36.6
[Ni([14]aneN ₄)] ²⁺ -NaY	70	54.7	66.6	33.4
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺ -NaY	70	70.1	71.9	28.1
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺ -NaY ^a	70	69.8	72.7	27.3
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺ -NaY ^b	70	69.1	71.7	28.3
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺ -NaY ^c	70	68.3	71.9	28.1
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺	40	2.9	75.9	24.1
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺	50	7.5	74.3	25.7
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺	60	16.9	72.5	27.5
[Ni(Bzo ₂ [12]aneN ₄)] ²⁺	80	44.9	68.1	31.9
[Ni(Bzo ₂ [14]aneN ₄)] ²⁺ -NaY	70	58.9	72.3	27.7

^a First reuse^b Second reuse^c Third reuse

To investigate the effect of temperature on the reactivity and product selectivity of catalyst, the oxidations were carried out only at temperatures >40 °C. The results have been shown in Table 3. At temperatures ranging from 40 °C to 80 °C for $[\text{Ni}(\text{Bzo}_2[12]\text{aneN}_4)]^{2+}-\text{NaY}$, the reactivity and the product selectivity of the complex varies with the temperature. At 70 °C the conversion is 70.1% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-2-one is 71.9% and 28.1%, respectively, while at 40 °C, the conversion is 2.9% and the selectivity to 2-cyclohexen-1-ol and 2-cyclohexen-1-one is 75.9% and 24.1%, respectively. The typical trend shows that reactivity and the selectivity to 2-cyclohexen-1-ol are decreased with the temperature in the range of 40 °C to 70 °C.

In summary, the results show that the “neat” complexes can be encapsulated in the nanopores of zeolite by template condensation between pre-entrapped $[\text{Ni}(\text{N}-\text{N})_2]^{2+}$ complexes and diethyloxalate. The “neat” and zeolite-Y-encapsulated nickel(II) tetraaza tetraone macrocyclic complexes exhibit efficient catalytic activity in the oxidation of cyclohexene using O_2 . The encapsulated complexes exhibit enhanced activity and selectivity in the oxidation reaction. The size of the macrocyclic ring and substitution also influence the catalytic activity. These encapsulated systems offer structural integrity by having a uniform distribution of the metal complex in the pore structure of the support. The zeolite framework keeps the guest complexes dispersed and prevents their dimerization leading to the retention of catalytic activity. Future work on this system is expected to envisage its industrial applications for partial oxidation reactions.

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