Synthesis, characterization and liquid phase oxidation of cyclohexanol using *tert*-butylhydroperoxide over host (zeolite-Y)/guest (copper(II) complexes of 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligand) nanocomposite materials (HGNM)

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Abstract

Nanocavity microreactor containing 12- and 13-membered diaza dioxa Schiff-base copper(II) complexes have been prepared by the one-pot template synthesis of (1,8-diamino-3,6-dioxaoctane)copper(II) with bifunctional diketone within the pores of zeolite-Y. The copper(II) complexes were entrapped in the supercage of Y-zeolite by a two-step process in the liquid phase: (i) inclusion of a copper(II) precursor complex, $[Cu(1,8$-diamino-3,6-dioxaoctane$)]^{2+}$-NaY and (ii) template condensation of the copper(II) precursor complex with the bifunctional diketone. Encapsulated copper(II) complex is catalytically very efficient as compared to other neat complexes for oxidation of cyclohexanol with *tert*-butylhydroperoxide (TBHP) as oxidant and is stable to be recycled without much deterioration.
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1. Introduction

Oxifunctionalization of alcohols to aldehydes and ketones is one of the widely used chemical transformations in organic synthesis as these products are important precursors or intermediates in the synthesis of many drugs, vitamins and fragrances [1,2]. A number of methods are known for alcohol oxidation [3], however, the development of newer methods and methodologies is gaining much attention currently due to the significance of this reaction. Even though various methods are now known, the most common methods still use toxic, corrosive and expensive oxidants such as chromium(VI) and manganese complexes, stringent conditions of high pressure or temperatures and use of strong mineral acids [1,4]. Oxidation over metal catalysts using eco-friendly oxidants such as H_2O_2 and O_2 are preferred now for environmental and economical benefits. Many of the methods using molecular oxygen require the presence of at least a stoichiometric amount of a reactive aldehyde that forms peracid as the actual oxidizing agent [5,6]. There are more effective aerobic oxidation methods that use copper [7,8], palladium [9,10] and ruthenium compounds [11].

The heterogeneous oxidation catalysis of alcohols with an environmentally suitable oxidant, H_2O_2, is quite an interesting objective for both the academic and industrial fields. Among the newer heterogeneous oxidation, catalysts attracting interest are copper containing porous and nonporous materials, such as Cu^{2+}-phthalocyanine incorporated inside Y faujasite and MCM-41 [12], Cu-HMS [13], Cu^{2+}-substituted MCM-41 [14], zeolite-encapsulated Cu^{2+}-salens [15], Cu^{2+}/X and Y-zeolite [16], $Cu(OH)_2$/silica [17] and *cis*-bisglycianato $Cu^{2+}/1,6$-naphthalenediol oligomer [18], which have been shown to be active for selective oxidations of a variety of organic compounds in the presence of hydrogen peroxide or organic peroxide.

In this paper, we report the synthesis and characterization of copper(II) complexes of 12- and 13-membered diaza dioxa Schiff-base macrocyclic ligand, 1,4-diaza-7,10-dioxacyclodo-
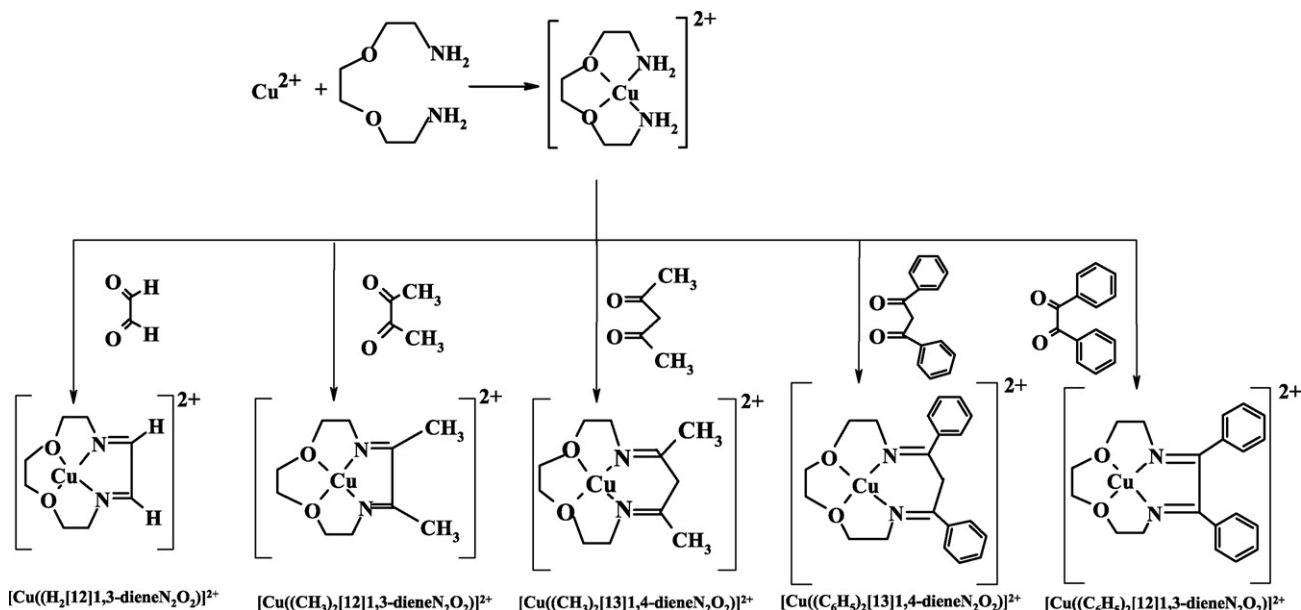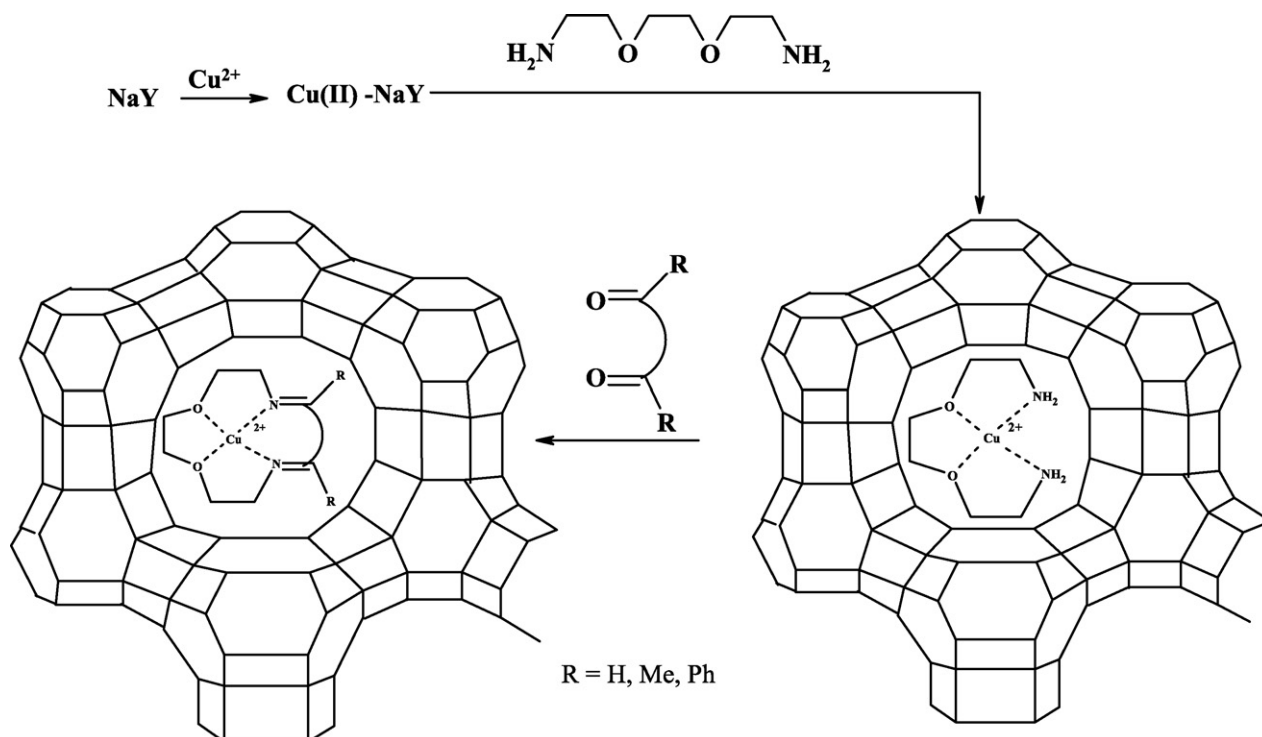
Scheme 1.

deca-1,3-diene, $H_2[12]1,3$-dieneN_2O_2; 2,3-dimethyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(CH_3)_2[12]1,3$-dieneN_2O_2; 2,3-diphenyl-1,4-diaza-7,10-dioxacyclododeca-1,3-diene, $(C_6H_5)_2[12]1,3$-dieneN_2O_2; 2,4-dimethyl-1,5-diaza-8,11-dioxacy-clotrideca-1,4-diene, $(CH_3)_2[13]1,4$-dieneN_2O_2; 2,4-diphenyl-1,5-diaza-8,11-dioxacyclotrideca-1,4-diene, $(C_6H_5)_2[13]1,4$-dieneN_2O_2, encapsulated within the nanodimensional pores of zeolite-Y by the one-pot template condensation of (1,8-diamino-3,6-dioxaoctane)copper(II) with bifunctional diketone shown in Schemes 1 and 2. Also, we report here the oxidation of

cyclohexanol catalyzed by host–guest nanocomposite material (HGNM) with hydrogen peroxide as oxygen donor.

2. Experimental

2.1. Materials and physical measurements

Safety note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution. All other reagents and solvent were purchased

Scheme 2.

from Merck (pro-analysis) and was dried using molecular sieves (Linda 4 Å). NaY with the Si:Al ratio of 2.53 was purchased from Aldrich (Lot No. 67812). After completely destroying the zeolitic framework with hot and concentrated HCl, sodium, aluminum and copper were analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100–1319), and SiO_2 was determined by gravimetric analysis. 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). Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 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 Kα radiation. Nitrogen adsorption measurements were performed at 77 K using a Coulter Omnisorb 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 [19,20]. 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. [Cu(1,8-diamino-3,6-dioxaoctane)]$(ClO_4)_2$ was obtained by the reaction of 1,8-diamino-3,6-dioxaoctane with $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol and recrystallized from water [21].

2.2. Preparation of [Cu(R₂[12]1,3-dieneN₂O₂)](ClO₄)₂ and [Cu(R₂[13]1,4-dieneN₂O₂)](ClO₄)₂ complexes

To a solution of (1,8-diamino-3,6-dioxaoctane)copper(II) perchlorate (5 mmol); [Cu(1,8-diamino-3,6-dioxaoctane)]$(ClO_4)_2$; in MeOH (100 cm³), solution of bifunctional diketone (glyoxal, 2,3-butanedione, 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione, benzil; 5 mmol) in MeOH (50 cm³) was added and the resulting mixture was stirred for ca. 26 h at reflux. The solid product was filtered off, washed with CH_3Cl and dried over fused $CaCl_2$ in desiccators. The product was crystallized from hot MeOH. Anal. calcd. for [Cu(H₂[12]1,3-dieneN₂O₂)]$(ClO_4)_2$: C, 22.20; H, 3.26; N, 6.47; C/N, 3.43; Cu, 14.68. Found: C, 21.96; H, 3.13; N, 6.59; C/N, 3.33; Cu, 14.51%; yield: ∼56%; $\upsilon_{C=N}$, 1612 cm^{-1}; d ↔ d, 580 nm; μ_B, 1.74 B.M; Λ_M, 267 (Ω^{-1} cm^{-1} M^{-1}). Anal. calcd. for [Cu((CH₃)₂[12]1,3-dieneN₂O₂)]$(ClO_4)_2$: C, 26.06; H, 3.94; N, 6.08; C/N, 4.29; Cu, 13.79. Found: C, 25.88; H, 3.78; N, 6.24; C/N, 4.15; Cu, 13.58%; yield: ∼53%; $\upsilon_{C=N}$, 1609 cm^{-1}; d ↔ d, 582 nm; μ_B, 1.73 B.M; Λ_M, 264 (Ω^{-1} cm^{-1} M^{-1}). Anal. calcd. for [Cu((C₆H₅)₂[12]1,3-dieneN₂O₂)]$(ClO_4)_2$: C, 41.07; H, 3.79; N, 4.79; C/N, 8.57; Cu, 10.86. Found: C, 40.88; H, 3.60; N, 4.91; C/N, 8.32; Cu, 10.69%; yield: ∼40%; $\upsilon_{C=N}$, 1618 cm^{-1}; d ↔ d, 576 nm; μ_B, 1.75 B.M; Λ_M, 257 (Ω^{-1} cm^{-1} M^{-1}). Anal. calcd. for [Cu((CH₃)₂[13]1,4-dieneN₂O₂)]$(ClO_4)_2$: C, 27.82; H, 4.25; N, 5.90; C/N, 4.72; Cu, 13.38. Found: C, 27.61; H, 4.10; N, 6.04; C/N, 4.57; Cu, 13.23%; yield: ∼55%; $\upsilon_{C=N}$, 1607 cm^{-1}; d ↔ d, 583 nm;

μ_B, 1.74 B.M; Λ_M, 253 (Ω^{-1} cm^{-1} M^{-1}). Anal. calcd. for [Cu((C₆H₅)₂[13]1,4-dieneN₂O₂)]$(ClO_4)_2$: C, 42.11; H, 4.04; N, 4.68; C/N, 9.00; Cu, 10.61. Found: C, 41.93; H, 3.90; N, 4.82; C/N, 8.70; Cu, 10.49%; yield: ∼39%; $\upsilon_{C=N}$, 1616 cm^{-1}; d ↔ d, 577 nm; μ_B, 1.73 B.M; Λ_M, 248 (Ω^{-1} cm^{-1} M^{-1}).

2.3. Preparation of [Cu(R₂[12]1,3-dieneN₂O₂)]²⁺-NaY and [Cu(R₂[13]1,4-dieneN₂O₂)]²⁺-NaY (R = H, Me and Ph)

Typically, a 4 g sample of NaY zeolite was mixed with 0.37 g of [Cu(1,8-diamino-3,6-dioxaoctane)]$(ClO_4)_2$, suspended in 100 ml of methanol and then refluxed for 8 h. The blue solid consisting of [Cu(1,8-diamino-3,6-dioxaoctane)]$^{2+}$ exchanged with Na$^+$ in NaY and denoted as [Cu(1,8-diamino-3,6-dioxaoctane)]$^{2+}$-NaY was collected by filtration, washed with ethanol and then dried at 80 °C under vacuum for 14 h. Then, to a stirred methanol suspension (100 ml) of [Cu(1,8-diamino-3,6-dioxaoctane)]$^{2+}$-NaY (2 g) were slowly added bifunctional diketone (glyoxal, 2,3-butanedione, 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione, benzyl) (3.65 mmol). The mixture was heated at reflux for 24 h until a pale blue suspension resulted. The solution was filtered and the resulting zeolites were Soxhlet extracted with N,N'-dimethylformamide (for 4 h), chloroform (for 6 h) and then with ethanol (for 3 h) to remove excess unreacted products from amine–aldehyde condensation and any copper(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting pale blue solids were dried at 90 °C under vacuum for 12 h. Anal. found for NaY: Si, 21.76; Al, 8.60; Na, 7.50; Si/Al, 2.53%; surface area, 545 m²/g; pore volume, 0.31 ml/g. Anal. found for Cu(II)NaY: Si, 21.45; Al, 8.48; Na, 4.47; Cu, 3.86; Si/Al, 2.53%; surface area, 532 m²/g; pore volume, 0.31. Anal. found for [Cu(H₂[12]1,3-dieneN₂O₂)]$^{2+}$-NaY: C, 5.63; H, 2.36; N, 1.75; C/N, 3.21; Cu, 2.84; Si, 21.17; Al, 8.37; Na, 5.34; Si/Al, 2.53%; $\upsilon_{C=N}$, 1608 cm^{-1}; surface area, 470 m²/g; pore volume, 0.27 ml/g; d ↔ d, 579 nm. Anal. found for [Cu((CH₃)₂[12]1,3-dieneN₂O₂)]$^{2+}$-NaY: C, 5.79; H, 2.40; N, 1.44; C/N, 4.01; Cu, 2.82; Si, 21.09; Al, 8.33; Na, 5.31; Si/Al, 2.53%; $\upsilon_{C=N}$, 1605 cm^{-1}; surface area, 466 m²/g; pore volume, 0.26 ml/g; d ↔ d, 580 nm. Anal. found for [Cu((C₆H₅)₂[12]1,3-dieneN₂O₂)]$^{2+}$-NaY: C, 8.66; H, 2.31; N, 1.04; C/N, 8.33; Cu, 2.64; Si, 20.91; Al, 8.26; Na, 5.28; Si/Al, 2.53%; $\upsilon_{C=N}$, 1610 cm^{-1}; surface area, 450 m²/g; pore volume, 0.23 ml/g; d ↔ d, 573 nm. Anal. found for [Cu((CH₃)₂[13]1,4-dieneN₂O₂)]$^{2+}$-NaY: C, 5.81; H, 2.42; N, 1.41; C/N, 4.48; Cu, 1.30; Si, 21.06; Al, 8.32; Na, 5.29; Si/Al, 2.53%; $\upsilon_{C=N}$, 1601 cm^{-1}; surface area, 460 m²/g; pore volume, 0.25 ml/g; d ↔ d, 581 nm. Anal. found for [Cu((C₆H₅)₂[13]1,4-dieneN₂O₂)]$^{2+}$-NaY: C, 8.70; H, 2.33; N, 1.00; C/N, 8.69; Cu, 2.62; Si, 20.87; Al, 8.25; Na, 5.26; Si/Al, 2.53%; $\upsilon_{C=N}$, 1607 cm^{-1}; surface area, 446 m²/g; pore volume, 0.21 ml/g; d ↔ d, 572 nm.

2.4. Oxidation of alcohols: general procedure

A mixture of 0.5 g catalysts and 30 mmol of cyclohexanol was stirred under nitrogen at 50 °C for 30 min. Then, 14 mmol of TBHP solution in di-tert-buthylperoxide was added. The result-

ing mixture was then refluxed for 8 h under nitrogen atmosphere. After filtration, the solid was washed with methylene chloride. The products then subjected to GC and GC-mass analysis using a Philips pu-4400 chromatograph (1.5 m, 3% OV-17 column), varian 3400 chromatograph (2.5 m, DB-5 column) coupled with a QP finnigan MATINCOF 50, 19 eV, respectively.

3. Results and discussion

The mononuclear diaza dioxa Schiff-base complexes, [Cu (H$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$, [Cu((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$, [Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$, [Cu ((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$, [Cu((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$, were readily prepared as the main product by the reaction of the (1,8-diamino-3,6-dioxaoctane)copper(II) with bifunctional diketone in a 1:1 molar ratio. The mononuclear complex can be readily isolated by fractional recrystallization of the product from *ca.* 0.05 M HClO$_4$ aqueous solutions. The molar conductance values of neat complexes ($\sim$267 Ω^{-1} mol^{-1} cm^2) and measured in water correspond to 1:2 electrolytes. The overall geometries of macrocyclic complexes have been deduced on the basis of the observed values of the magnetic moments ($\sim$1.73μ_B) and the band positions in the electronic spectra. The molecular formulae of the complexes have 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 copper contents of the catalysts were estimated by dissolving known amounts of the catalyst in conc. HCl and from these solutions, the copper contents were estimated using AAS. The chemical compositions confirmed the purity and stoichiometry of the neat and encapsulated complexes. The chemical analyses of the samples reveal the presence of organic matter with a C/N ratio roughly similar to that for neat complexes. The mol ratios Si/Al obtained by chemical analysis for zeolites are presented. The Si and Al contents in Cu(II)NaY and the zeolite complexes are almost in the same ratio as in the parent zeolite. The parent NaY zeolite has Si/Al molar ratio of 2.53 which corresponds to a until cell formula [Na$_{56}$[(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$]. The unit cell formula of metal-exchanged zeolites show a nickel dispersion of 10.8 moles per unit cell (Na$_{34.4}$Cu$_{10.8}$[(AlO$_2$)$_{56}$(SiO$_2$)$_{136}$]·nH$_2$O). The analytical data of each complex indicate Cu:C:N molar ratios almost close to those calculated for the mononuclear structure. This indicates little changes in the zeolite framework due to the absence of de-alumination in metal ion exchange.

The X-ray diffraction patterns of zeolite contained diaza dioxa complexes are similar to Cu(II)NaY and the parent NaY zeolite. This indicates that the crystallinity and morphology of zeolite was preserved during encapsulation. The surface area and micropore volume of the catalysts used in the oxidation reaction are investigated. The encapsulation of copper complexes reduced the surface area and adsorption capacity of zeolite. The lowering of the pore volume and surface area supported the fact

that complexes are present within the zeolite cages and not on the external surface.

The IR bands of heterogeneous catalysts occur at frequencies shifted within $\sim$8 cm^{-1} from those of the free complex; furthermore, some changes in band intensities can be observed in the region of the C=N ($\sim$1605 cm^{-1}) stretching vibration. These observation not only confirm the presence of copper(II) complex of 12- and 13-membered diaza dioxa macrocycle in the zeolite, but also suggest that its structure is not identical to that of the neat complex, thus stereochemically induced distortion of the complex, chemical ligation of the zeolite framework (NaY can act as a strong ligand), or some host–guest interactions (electrostatic) with the zeolite, can not be ruled out. The absorption bands in the $\sim$570 nm can be attributed to ligand–field transitions. This behavior is compatible with that observed for square-planar copper(II) complexes with two nitrogen and two oxygen donors [22–25]. The results are attributed to the electronic properties of the substituent group and are supported by similar observations with similar copper(II) N$_2$O$_2$ macrocycles [22–25].

In the preliminary phases, the reactivity of a model compound, the secondary cyclohexanol was examined under a variety of experimental conditions, Table 1. Table 1 shows the results of the oxidation of cyclohexanol with TBHP in the presence of zeolite with or without immobilized copper(II) complexes. The determining role played by the immobilized copper(II) or its complexes in zeolite is seen in Table 1 which shows the conversion percentages enhancement from 26.8% to more than 88.6% in the presence of Cu(II)NaY and [Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY, respectively (Table 1). The formation percentage of cyclohexanone is 100% no matter what kind of catalysis system is used.

The oxidation of cyclohexanol is negligible in the absence of transition metal catalysts confirming that under the conditions of the experiments, the oxidation is indeed catalytic in nature. In the case of the encapsulated catalysts, metal was not detected in the reaction products by AAS indicating that oxidation of cyclohexanol by dissolved metal complexes leached out from the zeolite matrix is negligible. The zeolites alone without the metal complexes were also catalytically inactive. Since the concentration of uncomplexed metal ions in the catalysts is also negligible, their contribution to catalytic activity may be neglected. Further evidence to confirm that the oxidation of cyclohexanol is indeed catalysed to a significant extent by the solid zeolite catalyst containing the encapsulated metal complex and not by the free complex dissolved in solution was obtained as follows: in one set of two identical experiments, the solid catalyst (Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY) was removed by centrifugation after a reaction time of 8 h. While the conversion of cyclohexanol proceeded further in the presence of the solid catalyst, there was no further conversion of cyclohexanol when the catalyst was removed from the reaction system. The following points may be noted:

1. 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,

Table 1
Oxidation of cyclohexanol with TBHP in the presence of copper(II) complexes

Catalyst	Conversion (%)	Selectivity (%)
[Cu(H$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	50.3	100
[Cu((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	47.6	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$	76.4	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$[a]	56.4	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$[b]	71.2	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$[c]	81.3	100
[Cu((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)](ClO$_4$)$_2$	44.5	100
[Cu((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)](ClO$_4$)$_2$	68.2	100
[Cu(H$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY	61.5	100
[Cu((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY	57.9	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY	88.6	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY[d]	87.9	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY[e]	87.1	100
[Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY[f]	86.6	100
[Cu((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY	57.2	100
[Cu((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY	79.7	100
Cu(ClO$_4$)$_2$·6H$_2$O	18.7	71
NaY	10.6	64
Cu(II)NaY	26.8	76

The concentrations were determined using internal standard procedure.
[a] Catalyst $= 0.5 \times 10^{-5}$ mol.
[b] Catalyst $= 2.04 \times 10^{-5}$ mol.
[c] Catalyst $= 4.08 \times 10^{-5}$ mol.
[d] First reuse.
[e] Second reuse.
[f] Third reuse.

while they were active in the first cycle, were completely destroyed during the first run and changed colour.

2. The neat complexes gave low conversions compared to the encapsulated catalysts. This may be a consequence of (1) above, since, due to the continuous degradation of the catalyst, the effective concentration of the catalyst will be lower than that taken initially.

3. The activity of cyclohexanol oxidation decreases in the series [Cu((C$_6$H$_5$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY > [Cu((C$_6$H$_5$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY > [Cu(H$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY > [Cu((CH$_3$)$_2$[12]1,3-dieneN$_2$O$_2$)]$^{2+}$-NaY > [Cu((CH$_3$)$_2$[13]1,4-dieneN$_2$O$_2$)]$^{2+}$-NaY.

4. At the end of reaction, the heterogeneous 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.

Comparison of our results with those obtained on the oxidation of cyclohexanol with TBHP either in the presence of K10-montmorillonite or 4A molecular sieves clearly indicate that our system is more efficient because of the presence of transition metal complexes encapsulated within nanodimensional pores of zeolite. In the absence of metal complexes, the reaction suffers from the disadvantage of higher reaction time [22]. The more activity of our catalysis system has clearly arisen from the existence of electron donating ligands which facilitate the electron transfer rate, a process that has previously been observed by us in other oxidation reactions [23,24]. This effect is increased in the case of aromatic ligand, which leads to the highest oxidation conversion percentages.

In summary, we have shown that copper complexes encapsulated within nanocavity of zeolite-Y coupled with TBHP, as oxidant is a very active catalyst for the oxidation of cyclohexanol. The high conversion percentage of about 88.6 with 100% selectivity toward the formation of cyclohexanone, which is the precursor of caprolactam, an important raw material for the production of synthetic fibers is remarkable. Finally, the mild conditions, easy working up and the successful occurance of one stage oxidation in primary alcohol systems are promising.

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