

Host (nanocavity of zeolite-Y)–guest (tetraaza[14]annulene copper(II) complexes) nanocomposite materials: Synthesis, characterization and liquid phase oxidation of benzyl alcohol

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Received 2 August 2005; received in revised form 27 September 2005; accepted 27 September 2005

Available online 9 November 2005

Abstract

Copper(II) complexes with tetraaza[14]annulene ligands “5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradecine [Cu(Me₄R₂Bzo[14]tetraeneN₄)] (R=H, CH₃, Cl and NO₂)” have been prepared from the one-pot template condensation reaction of substituted-1,2-phenylenediamine (4-methyl-, 4-chloro-, 4-nitro-1,2-phenylenediamine) with 2,4-pentanedione in the presence of copper(II) ion within the nanocavity pores of zeolite-Y “[Cu(Me₄R₂Bzo[14]tetraeneN₄)]–NaY”. The new materials were characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV/vis, XRD, BET and DRS). The analytical data indicated a composition corresponding to the mononuclear complex of tetraaza[14]annulene. The characterization data showed the absence of extraneous complexes, retention of zeolite crystalline structure and encapsulation in the nanocavities. Encapsulated copper(II) complex is catalytically very efficient as compared to other neat complexes for the partial oxidation of benzyl alcohol and is stable to be recycled without much deterioration.

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Keywords: Nanocavity; Zeolite-Y; Encapsulation; Copper(II); Template; Oxidation; Nanocomposite

1. Introduction

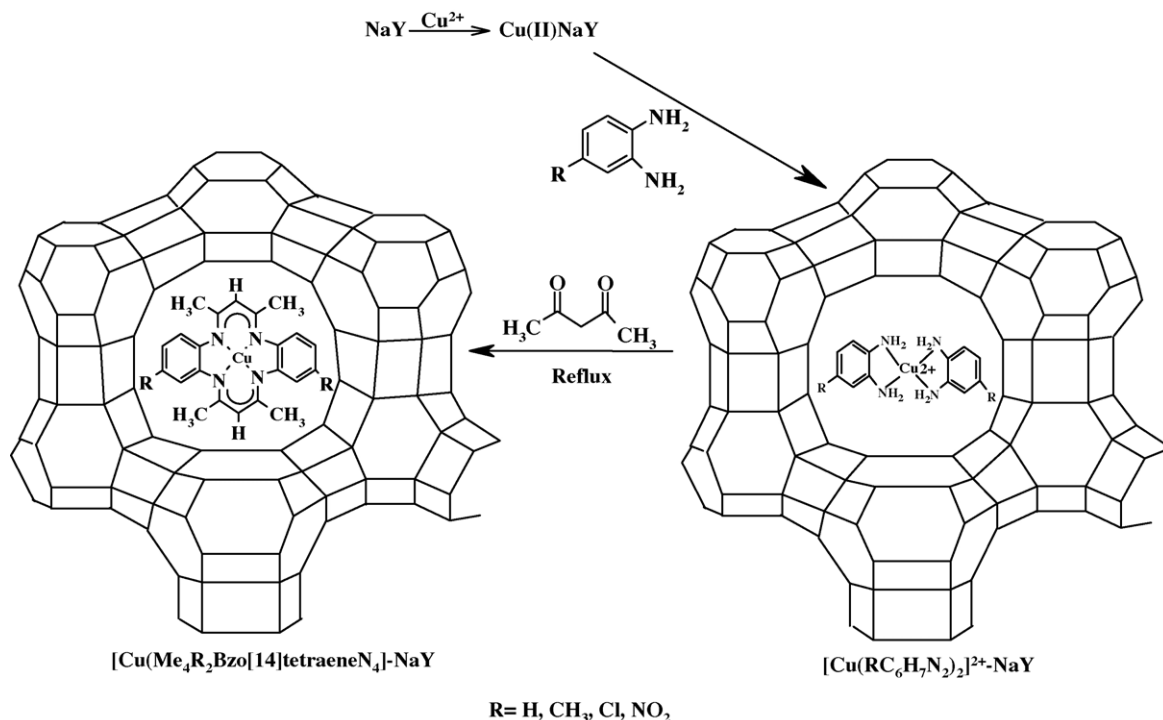
Nanocavity of zeolite encapsulated metal complexes is one of the subjects of the current catalysis research due to their potentiality as biomimetic heterogeneous catalysts for the oxidation of alkanes, alkenes and alcohols [1–15]. The as-prepared hybrid inorganic–organic material not only has heterogeneous catalysis characteristics, but also retains high catalytic efficiency originating in homogeneous catalysis due to the “*site isolated effect*”. These encapsulated catalysts are often referred to as *zeozymes* as they behave functionally similar to many enzyme catalysts in some selective oxidation. They possess the advantages of solid heterogeneous catalysts like easy separation, ruggedness, etc., share many advantageous features of homogeneous catalysts and minimize the disadvantages of both. In addition, the steric constraints imposed on the transition metal complex by zeolite channels, the negative charge of the zeolite framework and dis-

tribution of the positive charge of the cations as well as surface properties of the zeolite can also lead to specific interactions, inducing structural and functional modification, as compared to pure complexes [16–19].

In previous paper, we reported a series of complexes with polyaza macrocyclic ligands, by the template condensation of diamine, formaldehyde and amine in the presence of metal salt [4,23]. Also, we have reported the synthesis and characterization of copper(II) and nickel(II) complexes of 14- and 18-membered polyaza macrocyclic ligand encapsulation within the nanocavity of Y-zeolite by the one-pot template condensation reaction. In this paper, I report the synthesis and characterization of copper(II) complexes of 14-membered tetraaza macrocyclic ligands “5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradecine [Cu(Me₄R₂Bzo[14]tetraeneN₄)] (R=H, CH₃, Cl and NO₂)” encapsulated within the nanocavities of Y-zeolite by the template reactions of 4-substituted-1,2-phenylenediamine (4-methyl-, 4-chloro-, 4-nitro-1,2-phenylenediamine) with 2,4-pentanedione [Cu(Me₄R₂Bzo[14]tetraeneN₄)]–NaY, shown in **Scheme 1**, and used in the oxidation of benzyl alcohol with hydrogen peroxide as oxygen donor.

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Scheme 1.

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 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 SiO₂ 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 K α 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 [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.

2.2. Preparation of [Cu(RC₆H₇N₂)₂](ClO₄)₂ (R = H, CH₃, Cl and NO₂)

The complexes “[Cu(RC₆H₇N₂)₂](ClO₄)₂” were prepared according to the similar reported procedure of [Cu(en)₂](ClO₄)₂ [21].

2.3. Preparation of [Cu(Me₄R₂Bzo[14]tetraeneN₄)] (R = H, CH₃, Cl and NO₂)

The neat complexes were prepared according to literature through the well-know, as follows. A 100 ml round-bottomed flask was charged with a stirbar, Cu(OAc)₂·4H₂O (2.00 g, 8.03 mmol), substituted-1,2-phenylenediamine (4-methyl-, 4-chloro-, 4-nitro-1,2-phenylenediamine) (16.0 mmol), dry butan-1-ol (30 ml), and acetylacetone (1.7 ml, 17 mmol) added by syringes. The flask was set up in an oil bath on a hot plate stirrer (alternatively a heating mantle may be used instead, but a few boiling chips must be added) and equipped with a reflux condenser. The mixture was brought to a brisk reflux and stirred under reflux for 3 h, noting any color changes. (It is especially important to stir well in the initial stage of the reaction before all of the reagents have dissolved.) The flask was removed from the heat source and allowed to cool until just warm to touch (~30 °C). Methanol (30 ml) was added and the mixture was cooled in an ice-salt bath for at least 15 min to precipitate the non-polar macrocyclic complex (overnight cooling at -4 °C gives

much higher yield (about 65%). The mixture was filtered onto a glass frit and washed with MeOH (about 2 ml \times 10 ml; the washings should be colorless to pale green) to give dark purple microcrystal.

2.4. Preparation of Cu(II)–NaY

A 2 g NaY zeolite was suspended in 100 ml distilled water, which contained copper(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 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 atomic absorption spectrophotometer.

2.5. Preparation of [Cu(Me₄R₂Bzo[14]tetraeneN₄)]–NaY

For preparation of [Cu(Me₄R₂Bzo[14]tetraeneN₄)]–NaY; to a stirred methanol solution of Cu–NaY (4 g) was added 0.37 g of 1,2-phenylenediamine suspended in 100 ml of methanol and then refluxed for 8 h. The light yellow solid consisting of [Cu(RC₆H₇N₂)₂]²⁺ denoted as [Cu(RC₆H₇N₂)₂]²⁺–NaY was collected by filtration, washed with ethanol and then dried at 80 °C under vacuum for 14 h. To a stirred methanol suspension (100 ml) of [Cu(RC₆H₇N₂)₂]²⁺–NaY (2 g) were slowly added 2,4-pentanedione. The mixture was heated at reflux 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 4 h) and then with ethanol (for 3 h) to remove excess unreacted products from amine-aldehyde condensation and any Cu(II) complexes adsorbed onto the external surface of the zeolite crystallites. The resulting solids were dried at 90 °C under vacuum for 12 h. The remaining bis(substituted 1,2-phenylenediamine)copper(II) ions in zeolite were removed by exchanging with aqueous 0.1 M NaNO₃ solutions.

2.6. Catalytic activity measurements

The catalytic reaction was carried out in a thermostatic reactor of 100 ml volume equipped with a reflux condenser at the neck. The reaction mixture consisting of 50 mg catalyst, 5.0 ml of benzyl alcohol, 10 ml of benzene and hydrogen peroxide required to keep the oxidant to benzyl alcohol molar ratio at 2.0 was shaken for 8 h at the specified temperature. After the reaction, the organic layer was separated and the traces of substrate and product in aqueous layer were collected by extracting with diethyl ether. The components 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. The catalyst in the reaction mixture was filtered, washed with acetone and reused for the reaction at identical conditions to check the recycling ability. After this test, the catalyst was filtered and subjected to IR analysis to identify changes, if any, in the coordination environment.

3. Results and discussion

3.1. Synthesis and characterization of [Cu(Me₄R₂Bzo[14]tetraeneN₄)]–NaY (R = H, CH₃, Cl and NO₂)

The macrocyclic ligand “5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradecine”, a dianion which is usually abbreviated H₂tmtaa, shares many common characteristics with porphyrins, but it features some important differences. Thus, while it is of bioinorganic interest, it also has many other characteristics that make it of fundamental interest in its own right. The similarities to porphyrins are as follows: (1) the four nitrogen atoms of H₂tmtaa are confined to a plane, as in the porphyrins; (2) upon metal complexation, the ligand usually deprotonates to give a dianion and (3) tmtaa has a completely conjugated system of double bonds. The differences between tmtaa and the naturally occurring systems, however, account for the non-bioinorganic interest and hence for the proliferation of new and interesting compounds. The 14-membered ring size of tmtaa, as compared to a 16-membered one in porphyrins, favors shorter metal–nitrogen distances. Secondly, in contrast to the completely delocalized framework of porphyrins, each of tmtaa’s two negative charges tends to be localized only over the 2,4-pentanediiimino chelate rings. Lastly, even though tmtaa can be described as conjugated, it is anti-aromatic (4*n*) system, whereas porphyrins exhibit a 4*n* + 2*π* electron aromaticity. Tetraaza[14]annulene was first synthesized by Jager [22,23] via a template condensation reaction. Its modified synthesis and a crystal structure were reported much later by Goedken and co-workers [24,25].

The chemical compositions (Table 1) confirmed the purity and stoichiometry of the neat and nanocavity 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 that for neat complexes. In Table 1 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. 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 those of Cu(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 (FLS)” (Scheme 1) lead to the encapsulation of Cu(II) complexes of tetraaza ligand inside the zeolite nanopore. The results of chemical analyses of the samples are given in Table 1. 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 show a copper dispersion of 10.8 mol per unit cell (Na_{34.4}Cu_{10.8}[(AlO₂)₅₆(SiO₂)₁₃₆]·*n*H₂O). The analytical data of each complex indicate Cu:C:N molar ratios almost close to those calculated for the mononuclear structure.

Table 1
Chemical composition, DRS absorption and IR stretching frequencies of neat and zeolite-encapsulated copper(II) complexes^a

Sample	C (%)	H (%)	N (%)	C/N	Si (%)	Al (%)	Na (%)	Cu (%)	Si/Al	$\nu_{C=N}$ (cm^{-1})	Surfac area (m^2/g) ^b	Pore volume (mL/g) ^c	d ↔ d (cm^{-1})
NaY					21.76	8.60	7.50		2.53		545	0.31	
Cu(II)–NaY					21.45	8.48	4.47	3.86	2.53		532	0.31	
[Cu{C ₆ H ₈ N ₂ } ₂](ClO ₄) ₂	30.08 (29.91)	3.37 (3.26)	11.70 (11.83)	2.57 (2.53)				13.27 (13.16)					15160 ^d
[Cu{C ₆ H ₈ N ₂ } ₂] ²⁺ –NaY	5.11	1.05	2.12	2.41	21.45	8.48	5.65	2.99	2.53		489	0.28	15350
[Cu{(CH ₃)C ₆ H ₇ N ₂ } ₂](ClO ₄) ₂	33.18 (33.06)	3.98 (3.83)	11.06 (1.80)	3.00 (2.97)				12.54 (12.42)					15100 ^d
[Cu{(CH ₃)C ₆ H ₇ N ₂ } ₂] ²⁺ –NaY	5.14	1.13	1.80	2.85	21.44	8.47	5.64	3.01	2.53		478	0.25	15240
[Cu(ClC ₆ H ₇ N ₂) ₂](ClO ₄) ₂	26.32 (26.21)	2.58 (2.47)	10.23 (10.34)	2.57 (2.53)				11.60 (11.49)					15210 ^d
[Cu(ClC ₆ H ₇ N ₂) ₂] ²⁺ –NaY	5.08	1.06	2.12	2.40	21.45	8.48	5.64	3.05	2.53		475	0.27	15400
[Cu{(NO ₂)C ₆ H ₇ N ₂ } ₂](ClO ₄) ₂	25.34 (25.21)	2.48 (2.34)	14.78 (14.89)	1.71 (1.69)				11.17 (11.08)					15270 ^d
[Cu{(NO ₂)C ₆ H ₇ N ₂ } ₂] ²⁺ –NaY	5.06	1.04	3.33	1.52	21.43	8.47	5.65	2.98	2.53		470	0.24	15450
[Cu(Me ₄ Bzo[14]tetraeneN ₄)]	65.08 (94.90)	5.46 (5.35)	13.80 (13.92)	4.72 (4.66)				15.65 (15.51)		1647			15920 ^d
[Cu(Me ₄ Bzo[14]tetraeneN ₄)]–NaY	5.36	1.11	1.16	4.61	21.40	8.46	5.60	2.94	2.53	1650	428	0.25	16100
[Cu(Me ₄ (CH ₃) ₂ Bzo[14]tetraeneN ₄)]	66.41 (66.29)	6.04 (5.91)	12.91 (13.04)	5.14 (5.08)				14.64 (14.52)		1645			15880 ^b
[Cu(Me ₄ (CH ₃) ₂ Bzo[14]tetraeneN ₄)]–NaY	5.62	1.18	1.13	4.97	21.39	8.45	5.63	2.95	2.53	1647	421	0.22	16050
[Cu(Me ₄ Cl ₂ Bzo[14]tetraeneN ₄)]	55.63 (55.50)	4.24 (4.11)	11.80 (11.93)	4.71 (4.65)				13.38 (13.24)		1650			16000 ^b
[Cu(Me ₄ Cl ₂ Bzo[14]tetraeneN ₄)]–NaY	5.34	1.09	1.18	4.54	21.37	8.45	5.62	2.97	2.53	1653	423	0.24	16160
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]	53.27 (53.12)	4.06 (3.94)	16.94 (17.09)	3.14 (3.11)				12.81 (12.70)		1654			16080 ^b
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]–NaY	5.30	1.06	1.78	2.98	21.41	8.46	5.59	2.93	2.53	1657	417	0.21	16250

^a Calculated values are given in parentheses.

^b Surface area is the “monolayer equivalent area” calculated as explained in the Ref. [20].

^c Calculated by the *t*-method (see the text).

^d In chloroform solutions at 25 °C as never specified for neat complexes.

Electronic absorption data for the complexes (neat and encapsulated) are given in Table 1. The absorption bands appearing around $\sim 37040\text{ cm}^{-1}$ are attributed to $\pi \leftrightarrow \pi^*$ transitions within ligand molecules [26]. The absorption bands around $\sim 25640\text{ cm}^{-1}$ can be attributed to charge transfer (CT) transition from metal to ligand because the molar extinction coefficients are much larger than those normally assigned to ligand–field transitions [27]. The absorption bands in the $15150\text{--}16390\text{ cm}^{-1}$ range can be attributed to ligand–field transitions. This behavior is compatible with that observed for square-planar copper(II) complexes with four nitrogen donors [27,28]. The ligand–field transitions for encapsulated copper(II) complexes in nanocavity of zeolite-Y are compiled in Table 1. The results are attributed to the electronic properties of the substituent group and are supported by similar observations with copper(II) tetraaza N_4 macrocycles [29].

IR spectra of the neat complexes showed three intense bands about 1645 , 1530 and 1472 cm^{-1} in the $1400\text{--}1700\text{ cm}^{-1}$ range. A strong imine ($C=N$) absorption due to the macrocyclic framework was observed at 1645 cm^{-1} . Two absorptions due to the diiminate were observed at 1530 and 1472 cm^{-1} assignable to $\nu_{C=N}$ and $\nu_{C=C}$ but no ν_{N-H} absorption around 3200 cm^{-1} . The IR bands of zeolite-encapsulated copper(II) complexes occur at frequencies shifted within $\sim 4\text{--}6\text{ cm}^{-1}$ from those of the free complex; furthermore, some changes in band intensities can be observed in the region of the $C=N$ stretching vibration. These observations not only confirm the presence of copper(II) complex of 14-membered tetraaza 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, cannot be ruled out. The entrapped complexes exhibit very similar IR spectra with bands at all regions that are shifted $\sim 4\text{--}6\text{ cm}^{-1}$ relative to those of the corresponding free complexes. These vibrations in band frequency can also be attributed to: (i) distortions of the complexes, or to (ii) interactions with the zeolite matrix (by electrostatic effects or coordination—the higher negative charge of the zeolite host makes it a strong ligand) (Table 1).

The surface area and pore volume of the catalysts is presented in Table 1. The encapsulation of $[Cu(Me_4R_2Bzo[14]tetraeneN_4)]$ 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 $[Cu(Me_4R_2Bzo[14]tetraeneN_4)]$ complexes within the zeolite cages and not on the external surface.

3.2. Catalytic testing

The catalytic oxidation of alcohols into their corresponding aldehydes and ketones is an essential reaction in organic synthesis [30,31]. Traditional methods for performing such transformations generally involve the use of stoichiometric quantities of inorganic oxidants, e.g. Cr(VI), and generate large quantities of waste. The development of effective, greener catalytic systems that use clean, inexpensive oxidants, such as O_2 or

H_2O_2 to convert alcohols to carbonyl compounds is an important challenge [32]. One favorite oxidant to resort to is H_2O_2 due to its environmental impact, since water is the only by product of such oxidative reactions [33]. Although, a variety of different catalytic systems for the hydrogen peroxide oxidation of alcohols has been developed [34], there is a growing interest in the search for new efficient metal catalysts for this concern. Many molybdenum- and tungsten-based catalytic systems using hydrogen peroxide have been reported [35]. The oxidation of alcohols plays an important role in organic synthesis while the development of new oxidative processes continues drawing attention in spite of the availability of numerous oxidizing reagents. Such oxidizing reagents often used in stoichiometric amounts are often hazardous or toxic. Hence, in terms of economical and environmental concern, catalytic oxidation processes with inexpensive and environmental oxidants are extremely valuable.

The catalytic oxidation of benzyl alcohol was studied with $[Cu(Me_4R_2Bzo[14]tetraeneN_4)]-NaY$ ($R = H, CH_3, Cl$ and NO_2), using hydrogen peroxide as the oxidant. Blank reactions performed over NaY zeolite under identical conditions show only negligible conversion indicating that zeolite host is inactive for oxidation. Furthermore, hydrogen peroxide 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 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 tetraaza[14]annulene complexes and no significant role is played by either the zeolite support or free complexes.

Zeolite complexes were screened with respect to the activity for the oxidation of benzyl alcohol at 70°C and the results are shown in Tables 2 and 3. $[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]-NaY$ is distinctly better than other complexes for the oxidation. The activity was found to vary as $[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]-NaY > [Cu(Me_4Cl_2Bzo[14]tetraeneN_4)]-NaY > [Cu(Me_4Bzo[14]tetraeneN_4)]-NaY > [Cu(Me_4(CH_3)_2Bzo[14]tetraeneN_4)]-NaY$.

Table 2
Substrate conversion and product selectivity in the oxidation of benzyl alcohol with hydrogen peroxide in the presence of homogeneous tetraaza[14]annulene copper(II) complexes^a

Catalyst	Amount of catalyst (mg)	Conversion (%)	Selectivity (%)
$[Cu(Me_4Bzo[14]tetraeneN_4)]$	15	38.5	90.1
$[Cu(Me_4(CH_3)_2Bzo[14]tetraeneN_4)]$	15	23.8	88.6
$[Cu(Me_4Cl_2Bzo[14]tetraeneN_4)]$	15	51.5	95.7
$[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]$	10	50.5	100
$[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]$	15	57.5	100
$[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]$	20	53.6	97.6
$[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]$	25	45.9	95.7
$[Cu(Me_4(NO_2)_2Bzo[14]tetraeneN_4)]$	30	36.4	94.3

^a Conditions: benzyl alcohol = 5 ml, benzene = 10 ml, H_2O_2 /benzylalcohol molar ratio = 2, temperature = 70°C , reaction time = 8 h, the concentrations were determined using internal standard procedure.

Table 3

Substrate conversion and product selectivity in the oxidation of benzyl alcohol with hydrogen peroxide in the presence of tetraaza[14]annulene copper(II) complexes within the nanocavity pores of zeolite-Y^a

Catalyst	Amount of catalyst (mg)	Temperature (°C)	Conversion (%)	Selectivity (%)
[Cu(Me ₄ Bzo[14]tetraeneN ₄)]-NaY	50	70	64.3	100
[Cu(Me ₄ (CH ₃) ₂ Bzo[14]tetraeneN ₄)]-NaY	50	70	49.8	100
[Cu(Me ₄ Cl ₂ Bzo[14]tetraeneN ₄)]-NaY	50	70	78.4	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	20	70	46.5	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	30	70	58.6	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	40	70	77.4	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	50	70	82.3	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	60	70	83.1	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	50	40	13.7	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	50	50	48.5	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY	50	60	67.1	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY ^b	50	70	81.0	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY ^c	50	70	79.8	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY ^d	50	70	79.1	100

^a Conditions: benzyl alcohol = 5 ml, benzene = 10 ml, H₂O₂/benzylalcohol molar ratio = 2, reaction time = 8 h, the concentrations were determined using internal standard procedure.

^b First reuse.

^c Second reuse.

^d Third reuse.

The oxidation reactions may involve the coordination of oxygen atoms at the vacant sites of copper(II) in the complex [36]. This intermediate transfers the coordinated oxygen atoms to the substrate to obtain the product. Thus, the observed catalytic performance of the encapsulated complexes could be attributed to their geometries which govern the availability of vacant coordination sites.

[Cu(Me₄R₂Bzo[14]tetraeneN₄)]-NaY, the promising sample from the screening test, was further evaluated for catalytic activity for the oxidation of benzyl alcohol with hydrogen peroxide at various temperatures and the results are given in Table 3. The conversion in each case was found to increase with increasing reaction temperature. [Cu(Me₄R₂Bzo[14]tetraeneN₄)] as soluble catalysts (Table 2) are more prone to deactivation by the dimerization of active centers, which is expected to be reduced by encapsulating them in zeolites. [Cu(Me₄R₂Bzo[14]tetraeneN₄)]-NaY was recycled for the oxidation of benzyl alcohol with hydrogen peroxide with a view to establish the effect of encapsulation on stability. The initial run has showed a conversion of 82.3% and it is only marginally reduced to 79.1% on recycling the catalyst (third reuse). The results indicate that [Cu(Me₄R₂Bzo[14]tetraeneN₄)]-NaY are almost stable to be recycled for the oxidation of benzyl alcohol without much loss in activity (Table 3). Thus, the encapsulation of complexes in zeolites is found to increase the life of the catalyst by reducing dimerization due to the site isolation and 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 tetraaza[14]annulene after the oxidation reactions. It is interesting to note that the oxidation of benzyl alcohol with hydrogen peroxide over zeolite complexes leads to benzaldehyde as the exclusive product.

4. Conclusion

In summary, the results show that [Cu(Me₄R₂Bzo[14]tetraeneN₄)] can be encapsulated in the nanocavity of zeolite by template condensation between pre-entrapped [Cu(RC₆H₇N₂)₂]²⁺ complexes and 2,4-pentanedione. This strategy appears to be effective for the encapsulation of metal complexes with 14-membered tetraaza macrocycle ligands derived from [Cu(RC₆H₇N₂)₂]²⁺-NaY, as template condensation in the supercage is still possible and no unreacted [Cu(RC₆H₇N₂)₂]²⁺ ions were detected. Furthermore, the spectroscopic data suggest that the encapsulated complexes experience very little distortion in the nanocavity and that the chemical ligation to the zeolite surface is minimal. Nanocavity of zeolite-Y encapsulated copper(II) complexes of tetraaza[14]annulene are a novel solid catalyst system for the partial oxidation of benzyl alcohol. [Cu(Me₄(NO₂)₂Bzo[14]tetraeneN₄)]-NaY was found to be very active as compared to other complexes. 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 reaction. The following points may be noted:

1. The major product of oxidation of benzyl alcohol in this study is benzaldehyde.
2. The supported catalysts did not undergo any color change during the reaction and could be easily separated and reused many times. In contrast, the neat complexes active in the first cycle were completely destroyed during the first run and changed color.
3. The activity of benzyl alcohol oxidation decreases in the series: [Cu(Me₄(NO₂)₂Bzo[14]tetraeneN₄)]-NaY > [Cu(Me₄Cl₂Bzo[14]tetraeneN₄)]-NaY > [Cu(Me₄Bzo[14]-

tetraeneN₄)]–NaY > [Cu(Me₄(CH₃)₂Bzo[14]tetraeneN₄)]–NaY.

4. The conversion increase by several orders of magnitude when the copper(II) tetraaza[14]annulene are isolated from each other by encapsulation within the supercages of the faujasite zeolites.
5. The catalytic system is stable and can be recycled and reused several times without loss of activity.

Acknowledgements

I wish to express my indebtedness to Professor M.R. Ganjali from Tehran University for his continuous financial support this research. Also I would like to express my regret about the lack of any support from Kashan University especially the President of the University, Dr. H. Daghigh.

References

- [1] K.J. Balkus Jr., M. Eissa, R. Levado, *J. Am. Chem. Soc.* 117 (1995) 10753.
- [2] B. Zhan, X. Li, *Chem. Commun.* (1998) 349; G.D. Stucky, J.E. MacDougall, *Science* 274 (1990) 669; Y. Wang, N. Herron, *J. Phys. Chem.* 91 (1987) 257; N. Herron, *Inorg. Chem.* 25 (1986) 4714; B. Fan, W. Fan, R. Li, *J. Mol. Catal. A: Chem.* 201 (2003) 137; Á. Zsigmond, K. Bogár, F. Notheisz, *J. Catal.* 213 (2003) 103; Á. Zsigmond, A. Horváth, F. Notheisz, *J. Mol. Catal. A: Chem.* 171 (2001) 95; C. Schuster, W.F. Hölderich, *Catal. Today* 60 (2000) 193; A. Kozlov, A. Kozlova, K. Asakura, Y. Iwasawa, *J. Mol. Catal. A: Chem.* 137 (1999) 223; S.P. Varkey, C. Ratnasamy, P. Ratnasamy, *J. Mol. Catal. A: Chem.* 135 (1998) 295; K.J. Balkus, A.K. Khanmamedova, K.M. Dixon, F. Bedioui, *Appl. Catal. A: Gen.* 143 (1996) 159; M. Yoshizawa, T. Kusukawa, M. Fujita, K. Yamaguchi, *J. Am. Chem. Soc.* 122 (2000) 6311; N. Herron, Y. Wang, M. Eddy, G.D. Stucky, D.E. Cox, K. Moller, T. Bein, *J. Am. Chem. Soc.* 111 (1989) 530; K.O. Xavier, J. Chacko, K.K. Mohammed Yusuff, *J. Mol. Catal. A: Chem.* 178 (2002) 275.
- [3] I.L. Viana Rosa, C.M.C.P. Manso, O.A. Serra, Y. Iamamoto, *J. Mol. Catal. A: Chem.* 160 (2000) 199.
- [4] (a) M. Salavati-Niasari, *Chem. Lett.* 34 (2005) 244; (b) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 229 (2005) 159; (c) M. Salavati-Niasari, *Inorg. Chem. Comm.* 8 (2005) 174.
- [5] B. Fan, W. Fan, R. Li, *Stud. Surf. Sci. Catal.* 135 (2001) 7–10 (CD-ROM).
- [6] B. Fan, W. Cheng, R. Li, *Stud. Surf. Sci. Catal.* 135 (2001) 11–21 (CD-ROM).
- [7] S.P. Varkey, C. Ratnasamy, P. Ratnasamy, *J. Mol. Catal. A: Chem.* 135 (1998) 295.
- [8] Y. Umemura, Y. Minai, T. Tominaga, *J. Phys. Chem. B* 103 (1999) 647.
- [9] C.R. Jacob, S.P. Varkey, P. Ratnasamy, *Appl. Catal. A: Gen.* 182 (1999) 91.
- [10] T. Joseph, D.P. Sawant, C.S. Gopinath, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 184 (2002) 289.
- [11] V. Hulex, E. Dumitriu, F. Patcas, R. Ropot, P. Graffin, P. Moreau, *Appl. Catal. A: Gen.* 170 (1998) 169.
- [12] B.V. Romanovsky, *Proceedings of the Eighth International Congress on Catalysis*, Verlag Chiemie, Weinheim, 1984, p. 657.
- [13] N. Herron, G.D. Stucky, C.A. Tolman, *J.C.S. Chem. Commun.* (1986) 521.
- [14] T. Kimura, A. Fukuoka, M. Ichikawa, *Catal. Lett.* 4 (1990) 279.
- [15] R. Grommen, P. Manikandan, Y. Gao, T. Shane, J.J. Shane, R.A. Schoonheydt, B.M. Weckhuysen, D. Goldfarb, *J. Am. Chem. Soc.* 122 (2000) 11488.
- [16] D. Brunel, *Micropor. Mater.* 27 (1999) 329.
- [17] J.H. Clark, D.J. Macquarrie, *Chem. Commun.* (1998) 853.
- [18] (a) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 217 (2004) 87; (b) M. Salavati-Niasari, F. Farzaneh, M. Ghandi, *J. Mol. Catal. A: Chem.* 186 (2002) 101; (c) M. Salavati-Niasari, H. Banitaba, *J. Mol. Catal. A: Chem.* 201 (2003) 43; (d) M. Salavati-Niasari, J. Hasanalian, H. Najafian, *J. Mol. Catal. A: Chem.* 209 (2004) 204; (e) M. Salavati-Niasari, A. Amiri, *Appl. Catal. A: Gen.* 290 (2005) 46; (f) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 217 (2004) 87; (g) M. Salavati-Niasari, M.R. Elzami, M.R. Mansournia, S. Hydarzadeh, *J. Mol. Catal. A: Chem.* 221 (2004) 169; (h) M. Salavati-Niasari, P. Salemi, F. Davar, *J. Mol. Catal. A: Chem.* 238 (2005) 215; (i) M. Salavati-Niasari, T. Khosousi, S. Hydarzadeh, *J. Mol. Catal. A: Chem.* 235 (2005) 150.
- [19] (a) M. Salavati-Niasari, H. Najafian, *Polyhedron* 22 (2003) 2633; (b) M. Salavati-Niasari, M. Rezai-Adaryani, *Polyhedron* 23 (2004) 1325; (c) M. Salavati-Niasari, *Inorg. Chem. Commun.* 7 (2004) 698; (d) M. Salavati-Niasari, M. Rezai-Adaryani, S. Hydarzadeh, *Trans. Met. Chem.* 30 (2005) 445; (e) M. Salavati-Niasari, *J. Mol. Catal. A: Chem.* 217 (2004) 87; (f) M. Salavati-Niasari, *Inorg. Chem. Commun.* 7 (2004) 963; (g) M. Salavati-Niasari, A. Amiri, *Trans. Met. Chem.* 30 (2005) 720; (h) M. Salavati-Niasari, A. Amiri, *J. Mol. Catal. A: Chem.* 235 (2005) 114; (i) M. Salavati-Niasari, *Polyhedron* 24 (2005) 1405.
- [20] S.W. Wang, H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 57 (1985) 603; A. Lineares-Solano, Textural characterization of porous carbons by physical adsorption of gases, in: J.L. Figueiredo, J.A. Moulijn (Eds.), *Carbon and Coal Gasification*, Martinus Nijhoff, Dordrecht, M.A., 1986, p. 137.
- [21] J. Basset, G.H. Denney, G.H. Jeffery, J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis*, Wiley, New York, 1987, p. 429.
- [22] E.Z. Jager, *Anorg. Allg. Chem.* 76 (1966) 346.
- [23] E.Z. Jager, *Chemistry* 8 (1968) 392.
- [24] V.L. Goedken, J. Molin-Case, Y.-A. Whang, *Chem. Commun.* (1973) 337.
- [25] V.L. Goedken, J.J. Pluth, S.M. Peng, B. Bursten, *J. Am. Chem. Soc.* 98 (1976) 8014; V.L. Goedken, J.A. Ladd, *Chem. Commun.* (1982) 142.
- [26] (a) C.L. Bailey, R.D. Bereman, D.P. Rillema, R. Nowak, *Inorg. Chem.* 23 (1984) 3956; (b) A.R. Cutler, C.S. Alleyne, D. Dolphin, *Inorg. Chem.* 24 (1985) 2281; (c) C.L. Bailey, R.D. Bereman, D.P. Rillema, *Inorg. Chem.* 25 (1986) 3149; (d) K. Sakata, M. Hashimoto, T. Naganawa, *Inorg. Chem. Acta* 98 (1985) 11.
- [27] (a) B.N. Figgis, *Introduction to Ligand-Fields*, Wiley, New York, 1966; (b) A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984.
- [28] K. Sakata, M. Itoh, *J. Heterocycl. Chem.* 32 (1995) 329.
- [29] J.A. Steehy, D.G. Pillsbury, D.H. Busch, *Inorg. Chem.* 19 (1980) 3148.
- [30] T. Naota, H. Takaya, S.I. Murahashi, *Chem. Rev.* 98 (1998) 2599.
- [31] R.A. Sheldon, I.W.C.E. Arends, A. Dijkstra, *Catal. Today* 57 (2000) 157.
- [32] R.A. Sheldon, I.W.C.E. Arends, G.-J.T. Brink, A. Dijkstra, *Acc. Chem. Res.* 35 (2002) 774.
- [33] (a) G. Strukul (Ed.), *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer, Dordrecht, The Netherlands, 1992; (b) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, *J. Org. Chem.* 61 (1996) 8310–8311; (c) W.R. Sanderson, *Pure Appl. Chem.* 72 (2000) 1289.

- [34] (a) R. Neumann, M. Gara, *J. Am. Chem. Soc.* 117 (1995) 5066;
(b) I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1144.
- [35] (a) S.E. Jacobson, D.A. Muccigrosso, F.J. Mares, *Org. Chem.* 44 (1979) 921;
(b) B.M. Trost, Y. Masuyama, *Tetrahedron Lett.* 25 (1984) 173;
- (c) O. Bortolini, V. Conte, F. Furia, G.J. Modena, *Org. Chem.* 51 (1986) 2661;
(d) C. Venturello, M. Gambaro, *J. Org. Chem.* 56 (1991) 5924.
- [36] R.A. Sheldon, J.K. Kochi, *Metal-Catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981;
B. Meunier, *Bull. Soc. Chim. Fr.* (1986) 578.