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# Oxidation of benzyl alcohol and styrene using H<sub>2</sub>O<sub>2</sub> catalyzed by tetraazamacrocycle complexes of Cu(II) and Ni(II) encapsulated in zeolite-Y

# Vipin Kumar Bansal<sup>a</sup>, Pompozhi Protasis Thankachan<sup>a,\*</sup>, Rajendra Prasad<sup>b</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttrakhand, India

<sup>b</sup> School of Chemical Sciences, Faculty of Science and Technology, The University of the South Pacific, Suva, Fiji

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# ABSTRACT

Encapsulation of 7,16-diacetyl[ $M{Me_4(Bzo)_2[14]tetraeneN_4}$ ], {M = Cu(II) and Ni(II)} tetraazamacrocycle complexes in the cavity of Zeolite-Y by the template synthesis method has been described. These complexes have been characterized using various physico-chemical techniques viz., spectroscopic (electronic and IR) studies, thermal analysis, metal analysis, field emission scanning electron micrographs and X-ray powder diffraction patterns. These encapsulated tetraazamacrocycle complexes have been used as a heterogeneous catalyst for the oxidation of styrene and for the solvent free oxidation of benzyl alcohol using hydrogen peroxide as oxidant. The solvent free catalyzed oxidation of benzyl alcohol catalyzed by 7,16-diacetyl[ $Cu{Me_4(Bzo)_2[14]tetraeneN_4}$ ]-NaY gives benzaldehyde as the major product, while that of styrene gives benzaldehyde and styrene oxide as major oxidation products when 7,16-diacetyl[Ni{Me\_4(Bzo)\_2[14]tetraeneN\_4}]-NaY is used as catalyst.

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# 1. Introduction

Transition metal complexes show good catalytic activity and selectivity and therefore are widely used as homogeneous as well as heterogeneous catalysts in various chemical reactions [1–7]. The requirement of cheap and environment-friendly catalysts has biased research activity in favour of heterogeneous catalysts, due to their advantages over homogeneous catalysts such as easy separation from reaction mixture, selectivity and recyclability. For the heterogenization of a homogeneous catalyst various methods are used such as polymer anchoring [8,9], polymerization of homogeneous catalyst itself [10,11], immobilization of metal complex on a solid support like alumina, silica or zeolites [12-17] and covalently anchoring to multi-wall carbon nanotubes (MWNTs) [18]. Among these methods of heterogenization, encapsulation of metal complexes inside the supercages of zeolite has been found to be convenient and advantageous due to the selectivity, reusability and thermal and chemical stability. Generally speaking three approaches have been used for the preparation of zeolite encapsulated metal complexes. These are zeolite synthesis method (ZS), flexible ligand method (FL) and template synthesis method (TS). In ZS method, transition metal complexes, which are stable under the condition of zeolite synthesis such as high pH and high temperature, are added to the synthesis mixture. The resulting zeolite encapsulates the metal complexes in its cavity. In FL method if the size of ligand is smaller than the diameter of zeolite channels, the ligand is diffused freely through the zeolite channels. The ligand reacts easily with the desired metal ions which have been previously exchanged in the supercages of zeolite and makes a stable metal complex. When the ligand size is larger than the diameter of zeolite channels, then template synthesis (TS) method is used. In this method, the molecules of the ligand species are diffused freely into the zeolite cavity where they assemble around the resident metal ions (fixed by ion exchange) in the zeolite cavity. The size of the synthesized metal complex will be too large to escape out from the supercages of zeolite. These encapsulated metal complexes in the cavity of zeolite have been called by several research groups as "zeolite encapsulated metal complex (ZEMC)" or "ship-in-a-bottle" [19,20]. ZEMC catalysts behave functionally in a similar way to many enzyme catalysts and are often referred to as "zeozymes" [21,22]. Tetraazamacrocycle complexes of various metals were easily encapsulated in zeolite cavities and successfully used as heterogeneous catalyst in various oxidation reactions such as oxidation of phenol, styrene, benzyl alcohol, cyclohexene, cyclohexane and ethylbenzene [5,6,23-25].



<sup>\*</sup> Corresponding author. Tel.: +91 1332 285331; fax: +91 1332 273560. *E-mail address:* ppthnfcy@iitr.ernet.in (P.P. Thankachan).

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Oxidation of benzyl alcohol to benzaldehyde is an industrially important reaction. Chlorine free benzaldehyde is a versatile chemical intermediate widely used in the manufacture of pharmaceuticals, perfume and flavoring chemicals. The oxidation of styrene gives a variety of products such as carbonyl compounds, epoxides, diols and products of oxidative cleavage of C–C bond. Several research groups have developed different catalytic methods for oxidation of benzyl alcohol benzaldehyde and styrene. ZEMC catalysts are successfully employed for this purpose [26–32].

In this research, we have synthesized and characterized 7,16diacetyl[M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}], {M=Cu(II) and Ni(II)} tetraazamacrocycle complexes and encapsulated these complexes in the supercages of zeolite-Y by the template synthesis method. These complexes have been characterized by using various physico-chemical techniques viz. UV-vis, FT-IR, XRD, TG/DTA, AAS and FE-SEM. Catalytic activity of these encapsulated complexes towards oxidation of benzyl alcohol and styrene was investigated.

#### 2. Experimental

#### 2.1. Materials and methods

All common chemicals and solvents were of analytical grade and were purchased from Rankem (India). Benzyl alcohol, ophenylenediammine and 30%  $H_2O_2$  were purchased from Rankem (India). Nickel acetate, copper acetate, acetylacetone, triethylamine and acetylchloride were obtained from Loba Chemie (India). Styrene was obtained from Acros Organics (USA). Zeolite-Y (Si/Al ~2.53) obtained from Sud Chemie (India), was dried at 400 °C for 6 h before being used as host material for encapsulating complexes. The benzene used for the synthesis of acylated tetraazamacrocycle complexes was dried over sodium wire and distilled. Tetraazamacrocycle complexes [M(Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>)] {M = Cu(II) and Ni(II)} were prepared following the procedure described in the literature [33,34].

#### 2.2. Instrumentation and analysis

IR spectra of neat macrocycle complexes and zeolite encapsulated metal macrocycle complexes were recorded on a Thermo Nicolet-NEXUS Aligent 1100 FT-IR spectrometer in KBr. Electronic spectra of neat macrocycle complexes were recorded on a Shimadzu 1601 UV-vis spectrophotometer in chloroform, while electronic spectra of zeolite encapsulated metal macrocycle complexes were recorded in nujol by layering the mull of the sample inside one of cuvettes while keeping the other one layered with nujol as reference. The FAB mass spectra of neat acylated macrocycle complexes were recorded on a Jeol SX-102/DA-6000 mass spectrometer in 3-nitrobenzyl alcohol matrix using xenon as FAB gas. <sup>1</sup>H NMR was recorded on a Bruker DRX-500 spectrometer in chloroform-d. Elemental analyzes of neat tetraazamacrocycle complexes were carried out on an Elementar Vario EL-III analyzer. XRD patterns were recorded using a Bruker AXS D8 Advance X-ray powder diffractometer with a Cu K<sub> $\alpha$ </sub> target. TG/DTA of zeolite encapsulated macrocycle complexes were recorded using a TG Stanton Redcroft STA 780. Copper and nickel metals were analyzed using a Perkin-Elmer A Analyst 800 atomic absorption spectrometer after completely destroying the zeolite framework with hot and concentrated nitric acid and diluting with double distilled water to a specific volume. Field emission scanning electron micrographs of zeolite encapsulated tetraazamacrocycle metal complexes were recorded using a Quanta 200 FE-SEM instrument. The zeolite encapsulated tetraazamacrocycle metal complexes were coated with a thin film of gold before recording the FE-SEM to protect surface material from thermal damage by the electron beam. The identities of the reaction products were confirmed with a GC–MS model Perkin-Elmer Clarus 500. Catalyzed reactions were analyzed using a Hewlett Packard gas chromatograph model 5890 A, fitted with FID detector and a ( $30 \text{ m} \times 0.53 \text{ mm} \times 2.65 \mu \text{m}$ ) HP-1 capillary column.

#### 2.3. Preparations

#### 2.3.1. Preparation of complex

#### 7,16-diacetyl[Cu{ $Me_4(Bzo)_2$ [14]tetraeneN<sub>4</sub>}]

The complex  $[Cu{Me_4(Bzo)_2[14]tetraeneN_4}](0.5 g, 1.23 mmol)$ and acetyl chloride (0.3 ml, 4.2 mmol) were dissolved in 100 ml anhydrous benzene, followed by drop by drop addition of triethylamine (1.5 ml, 10.8 mmol), keeping the temperature at 0°C. The reaction mixture was protected from moisture and stirred for 2 h at 0-5 °C. The reaction mixture was allowed to stand at room temperature for 6 h and then filtered. The filtrate was evaporated to dryness under reduced pressure. The product was washed with hot water till the washings became colourless. The compound was dried at 75 °C in a vacuum oven. The dry residue was extracted in chloroform. The compound was purified by passage through a  $15 \text{ cm} \times 2.5 \text{ cm}$  alumina column eluting with chloroform. Three colored bands of two acylated products along with the parent compound were observed. The first and second bands were minor and were discarded. The third yellowish green band, eluted with chloroform, was collected. The bulk of the solvent was removed at reduced pressure. Fine dark violet crystals were obtained. Yield 0.34g (56.4%) m.p.>300 °C. Analyzes found C, 63.60; H, 5.23; N, 11.50%. C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Cu calcd.: C, 63.72; H, 5.35; N, 11.43%. UV-vis  $(in CHCl_3 \lambda_{max}, nm/\epsilon_{max}, Lmol^{-1} cm^{-1}); 636 (2029), 412 sh (20854),$ 380 (58593), 314 (21700), 285 (31454) and 252 (44770) IR (KBr pellet,  $\nu$ , cm<sup>-1</sup>):  $\nu$  (C=O) 1662 cm<sup>-1</sup>,  $\nu$ (N=C-C) 1531 cm<sup>-1</sup>,  $\nu$ (C=C) 1448 cm<sup>-1</sup> and  $\nu$ (=C-H) 1386 cm<sup>-1</sup>. FAB mass (*m*/*z*) [M+1]<sup>+</sup> 491, 490.06 (calcd. molecular weight).

#### 2.3.2. Preparation of complex

7,16-diacetyl[Ni{ $Me_4(Bzo)_2$ [14]tetraeneN\_4}]

For the synthesis of 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] the procedure adopted was similar to that described above except that the complex [Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] (0.49 g, 1.23 mmol) was used. Yield 0.41 g (68.7%) m.p. > 300 °C. Analyzes found C, 64.22; H, 5.41; N, 11.61%.  $C_{26}H_{26}N_4O_2Ni$  calcd.: C, 64.36; H, 5.40; N, 11.55%. UV-vis (in chloroform  $\lambda_{max}$ , nm/ $\varepsilon_{max}$ , Lmol<sup>-1</sup> cm<sup>-1</sup>); 585 (5728), 416sh (13205), 392 (36404), 335 (7089), 267 (29947), IR (KBr pellet,  $\nu$ , cm<sup>-1</sup>):  $\nu$ (C=O) 1646 cm<sup>-1</sup>,  $\nu$ (N=C-C) 1535 cm<sup>-1</sup>,  $\nu$ (C=C) 1434 cm<sup>-1</sup> and  $\nu$ (=C-H) 1380 cm<sup>-1</sup>. FAB mass (*m*/*z*) [M+1]<sup>+</sup> 486, 485.21 (calcd. molecular weight), <sup>1</sup>H NMR (in CDCl<sub>3</sub>):  $\delta$  2.04 (s 12H, CH<sub>3</sub>), 6.65–6.67 (m 8H, arom.), 2.53 ppm (s 6H, –COCH<sub>3</sub>).

#### 2.3.3. Preparation of M(II)-NaY {M = Cu(II) and Ni(II)}

A 4.0 g amount of NaY zeolite was taken in 300 ml of distilled water and to this cupric acetate (3.99 g, 20 mmol) was added for the preparation of Cu(II)-NaY/nickel acetate (4.98 g, 20 mmol) for Ni(II)-NaY was added. The reaction mixture was heated on an oil bath at 90 °C for 24 h with constant stirring. The reaction mixture was filtered off and washed with hot distilled water until the filtrate was from metal ion free (confirmed by AAS of filtrate). The solid residue was dried in an oven at 120 °C for 24 h. The ion exchange degree of the zeolite was determined with an atomic absorption spectrophotometer.

# 2.3.4. Preparation of $[M(C_6H_8N_2)_2]^{2+}$ -NaY {M = Cu(II) and Ni(II)}

For the preparation of  $[M(C_6H_8N_2)_2]^{2+}$ -NaY {M = Cu(II) and Ni(II)}, Cu(II)-NaY (2.0 g)/Ni(II)-NaY (2.0 g) and ophenylenediammine (0.38 g, 3.5 mmol) were mixed in 150 ml methanol in a round bottom flask. The reaction mixture was

refluxed on an oil bath for 20 h with constant stirring. The solid, consisting of zeolite encapsulated  $[Cu(C_6H_8N_2)_2]^{2+}$  denoted as  $[Cu(C_6H_8N_2)_2]^{2+}$ -NaY and zeolite encapsulated  $[Ni(C_6H_8N_2)_2]^{2+}$  denoted as  $[Ni(C_6H_8N_2)_2]^{2+}$ -NaY, was filtered. The solid was washed with methanol till the washings became colourless and then dried at 80 °C in vacuum oven for 24 h.

# 2.3.5. Preparation of [M(Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>)]-NaY {M = Cu(II) and Ni(II)}

Zeolite encapsulated complexes  $[M(C_6H_8N_2)_2]^{2+}-NaY$  $\{M = Cu(II) \text{ and } Ni(II)\}, 2.0 \text{ g each and acetylacetone } (0.4 \text{ ml},$ 3.8 mmol) were taken in 150 ml of methanol in a round bottom flask. The reaction mixture was refluxed in an oil bath with constant stirring for 24 h. Thus obtained mixture was filtered, washed with dichloromethane and dried for 20 h at 80 °C. The catalyst thus obtained was subjected to soxhlet extraction with dichloromethane, followed by acetonitrile for 12h to remove excess unreacted products and neat complex adsorbed on the surface of zeolite-Y .The uncomplexed copper and nickel metal ions present in the cavity and on the surface of zeolite were removed by stirring the compounds with aqueous 0.1 M NaCl solution for 12 h. The resulting solid was filtered and washed with distilled water until free from chloride ions (confirmed by adding AgNO<sub>3</sub> solution to the filtrate). The solid thus obtained was dried in a vacuum oven at 120 °C for 48 h to constant weight.

#### 2.3.6. Preparation of

7,16-diacetyl[M{ $Me_4(Bzo)_2[14]$ tetraene $N_4$ }]-NaY {M = Cu(II) and Ni(II)}

Zeolite encapsulated  $[M(Me_4(Bzo)_2[14]tetraeneN_4)]$ -NAY {M = Cu(II) and Ni(II)} (2g) was placed in 100 ml of anhydrous benzene in a round bottom flask. Triethylamine (3.9 ml, 28 mmol) was added to it. The reaction mixture was refluxed in an oil bath with constant stirring for 2 h. The reaction mixture was cooled to room temperature and acetylchloride (2 ml, 28 mmol) was added, and the reaction mixture was again refluxed for 4 h with constant stirring, protected from moisture. The products were filtered and washed with methanol and finally washed with hot water. The compound was dried in an oven at 90 °C for 24 h.

#### 2.4. Catalytic activity

# 2.4.1. Oxidation of benzyl alcohol

Solvent free catalytic oxidation of benzyl alcohol was carried out in a 50 ml round bottom flask fitted with a water circulated condenser using zeolite encapsulated Cu(II) tetraazamacrocycle complexes as catalyst. In a typical reaction, benzyl alcohol (3.24 g, 30 mmol) and 30%  $H_2O_2$  (5.10 g, 45 mmol) were mixed and the reaction mixture was heated in an oil bath with continuous stirring at 75 °C. An appropriate amount of catalyst (30 mg) was added to the hot mixture and the reaction was continued. The progress of the reaction was determined by analyzing the reaction mixture using a gas chromatograph by withdrawing small aliquots of the reaction mixture at specific interval of time. The identity of reaction products was confirmed by GC–MS.

# 2.4.2. Oxidation of styrene

The catalytic oxidation of styrene was carried out using zeolite encapsulated Ni(II) tetraazamacrocycle complexes as catalyst. Styrene (1.56 g, 15 mmol),  $H_2O_2$  (3.52 g, 30 mmol) and catalyst (35 mg) were taken in 10 ml of acetonitrile and the reaction was carried out at 70 °C in an oil bath with continuous stirring. The progress of reaction was determined as described above. The identity of the oxidation products was confirmed by GC–MS.

#### 3. Results and discussion

#### 3.1. Characterization of catalysts

The complexes 7,16-diacetyl[M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]  $\{M = Cu(II) \text{ and } Ni(II)\}\$  were synthesized by the acylation of  $[M{Me_4(Bzo)_2[14]tetraeneN_4}] {M=Cu(II) and Ni(II)} and char$ acterized by various physico-chemical techniques. Encapsulation of these tetraazamacrocycle complexes in the nanocavity of zeolite was carried out by template synthesis method, in which tetraazamacrocycle complexes were synthesized in the nanocavity of zeolite-Y. Encapsulation was carried out in three steps. In the first step, the desired metals nickel(II) and copper(II) were exchanged with the Na<sup>+</sup> ion of zeolite-Y. In the second step, the molecules that constitute the ligand species that make the complex in the nanocavity of zeolite with previously exchanged Ni(II) and Cu(II) metal were diffused in zeolite pores. The size of the synthesized metal complex will be too large to escape out from the supercages of zeolite. This process is called "ship-in-a-bottle". The uncomplexed metal ions in the nanocavity of zeolite as well as its surface if any were removed by exchanging the metal ion with 0.1 M NaCl aqueous solution. The complex synthesized at the surface of zeolite was removed by soxhlet extraction with dichloromethane followed by acetonitrile, so that the metal content found after analysis would be due to the presence of encapsulated metal macrocycle complex in the cavity of zeolite alone. Zeolite encapsulated complexes thus obtained were dried in a vacuum oven at 120 °C for 48 h to remove moisture. After that, acylation at the 7,16 positions of the tetraazamacrocycle complexes were carried out in the cavity of zeolite (Scheme 1). The percentage of metal ion after encapsulation in zeolite was determined by AAS. The percentage of metal content, molecular formula and colour is shown in Table 1.

# 3.2. Electronic spectral studies

The electronic spectrum of neat macrocycle complex 7,16diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] exhibits six bands at 636, 412, 380, 314, 285 and 252 nm (Table 2), while the 7,16diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] exhibits five bands at 585, 416sh, 392, 335 and 267 nm; these are in agreement with the literature values [35]. The absorption band observed above 435 nm are due to  $\pi \rightarrow \pi^*$  transitions within a ligand. The transitions observed at 585 nm in 7,16-diacetyl[Ni{Me\_4(Bzo)\_2[14]tetraeneN\_4}] and 636 nm in 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>} are attributed to d-d transitions due to Ni(II) and Cu(II). The spectral behavior of these complexes is consistent with that of square planar coordination of Ni(II) and Cu(II) [36]. The large molar absorbance of d-d transitions could be the result of intensity stealing from strong UV absorption bands [37]. All the encapsulated complexes exhibit the almost identical spectral patterns to those of their neat macrocycle complexes. Zeolite encapsulated 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] complexes exhibit spectral bands at 590, 397 and 265 nm while 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] complexes exhibit spectral bands at 642, 383, 286 and 242 nm (Fig. 1, Table 2). Precursors of these acylated complexes also show similar behavior [5,38]. The presence of these spectral bands in the electronic spectra of encapsulated complexes confirmed the existance of complexes in the cavity of zeolite-Y.

#### 3.3. FT-IR spectral studies

A partial list of IR spectral data of neat as well as zeolite encapsulated tetraazamacrocycle complexes has been given in Table 2. The intensity of IR bands in all zeolite encapsulated complexes is weak in comparison to those of the neat com-



Scheme 1.

mentioned intense bands were observed in the IR spectra of zeo-

lite encapsulated tetraazamacrocycle complexes. The IR spectrum

of neat zeolite-Y showed a strong broad band at 1634 cm<sup>-1</sup> due

to zeolite frame-work. In acylated zeolite encapsulated tetraaza-

macrocycle complexes this band shifts to a higher frequency due

to merging of C=O bands (shown in Table 2). These IR bands were

observed slightly frequency shifted by  $\sim 4-6 \,\mathrm{cm}^{-1}$ . These vari-

ations in the band frequency might be due to distortion in the

complexes or to interactions with the zeolite matrix. These obser-

plexes due to their low concentration in zeolite cavities. The IR spectrum of [Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>] showed three intense bands at 1547 (N=C-C), 1462 (C=C) and 1396 (=C-H) while and [Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>] showed bands at 1566 cm<sup>-1</sup> (N=C-C), 1447 cm<sup>-1</sup> (C=C) and 1403 cm<sup>-1</sup> (=C-H). Upon acylation of these complexes, a strong band due to C=O was observed at 1646 and 1662 cm<sup>-1</sup> respectively along with three intense bands with a slight shift. When acylated and precursor tetraazamacrocycle complexes are encapsulated in the zeolite cavity, the three above

#### Table 1

Chemical composition, physical and analytical data.

Compound	Metal content (wt.%)	Color		
Cu-NaY	3.91	Light blue-green		
Ni-NaY	4.16	Light green		
[Cu(Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> )]-NaY	2.23	Light-yellow		
[Ni(Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> )]-NaY	2.38	Greenish-yellow		
7,16-diacetyl[Cu{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }]-NaY	2.22	Light-yellow		
7,16-diacetyl[Ni{Me4(Bzo)2[14]tetraeneN4}]-NaY	2.37	Greenish-yellow		

#### Table 2

IR and electronics data of neat and zeolite encapsulated tetraazamacrocycle complexes.

Compound	$\lambda_{\max}$ (nm)	IR (cm <sup>-1</sup> )
$[Cu{Me_4(Bzo)_2[14]tetraeneN_4}]$	637, 414, 383, 315, 288, 250	1566, 1447, 1403
$[Ni{Me_4(Bzo)_2[14]tetraeneN_4}]$	586, 429sh, 395, 337, 270	1547, 1462, 1396
7,16-diacetyl[Cu{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }	636, 412, 380, 314, 285, 252	1662, 1531, 1448, 1386
7,16-diacetyl[Ni{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }]	585, 416sh, 392, 335, 267	1646, 1535, 1434, 1380
$[Cu{Me_4(Bzo)_2[14]tetraeneN_4}]-NaY$	642, 387, 286, 242	1635, 1538, 1456, 1401
[Ni{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }]-NaY	590, 397, 265	1634, 1544, 1458, 1394
7,16-diacetyl[Cu{Me4(Bzo)2[14]tetraeneN4}]-NaY	642, 383, 286, 242	1654, 1532, 1448, 1382
$7,16-diacetyl[Ni\{Me_4(Bzo)_2[14]tetraeneN_4\}]-NaY$	590, 397, 265	1643, 1533, 1426, 1378



 $\label{eq:Fig. 1. Electronic spectra of neat 7,16-diacetyl[CuMe_4(Bzo)_2[14]tetraeneN_4)] (A) and 7,16-diacetyl[Cu{Me_4(Bzo)_2[14]tetraeneN_4}]-NaY (B).$ 

vations confirm not only the acylation but also the presence of metal tetraazamacrocycle complexes in the cavities of zeolite.

# 3.4. Field emission scanning electron micrograph study

Field emission scanning electron micrographs (FE-SEM) of zeolite encapsulated tetraazamacrocycle complexes recorded before and after soxhlet extraction are shown in Fig. 2, which shows well defined crystals of zeolite encapsulated tetraazamacrocycle complexes after soxhlet extraction, free from any shadow of metal complex present on the external surface of zeolite. During the process of encapsulation and soxhlet extraction, the framework of the zeolite-Y was not damaged.

# 3.5. Powder X-ray diffraction studies

The powder X-ray diffraction (XRD) patterns of all zeolite encapsulated tetraaza macrocycle metal complexes, metal exchanged zeolite and zeolite-Y were recorded at  $2\theta$  values between 5 and  $40^{\circ}$  to see their crystallinity and to ensure encapsulation of metal complexes in the cavity of zeolite .The powder X-ray diffraction patterns of zeolite-Y, metal exchanged zeolite Cu(II)-NaY and zeolite encapsulated 7,16diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY metal complexes are shown in Fig. 3. The diffraction patterns of encapsulated tetraazamacrocycle complexes, Cu(II)-NaY and zeolite-Y are almost identical similar with only very slight changes. One new peak in the XRD pattern of 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and  $[Cu{Me_4(Bzo)_2[14]tetraeneN_4}]$ -NaY was detected at 2 $\theta$  value of 7.7. XRD patterns of 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY, [Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY, Ni(II)-Y and NaY were nearly identical. This new peak, observed in the XRD patterns of zeolite encapsulated metal macrocycle complexes may be due to encapsulation of metal complexes in the cavity of zeolite. Further, a little change occurred in the relative peak intensities of 331, 311 and 220 upon introducing the metal ions or macrocycle complexes. In neat zeolite-Y intensity values were found in the order  $I_{331} > I_{220} > I_{311}$ . Upon exchanging the metal or after, the encapsulation process affects the relative peak intensities of the 311and 220 peaks, the intensity being in the order  $I_{331} > I_{311} > I_{220}$ . This was attributed to a redistribution of intrazeolite charge balancingcations [39-41]. These observations indicate that the crystallinity of the zeolite has not undergone any significant change during the process of encapsulation. The analysis of FE-SEM image also supports the assertion that all the modified zeolite has retained the crystallinity of the zeolite-Y.



Fig. 2. Field emission scanning electron micrograph of 7,16-diacetyl[Ni{Me\_4(Bzo)\_2[14]tetraeneN\_4}]-NaY of before (A) and after (B) soxhlet extraction.

#### 3.6. Thermo gravimetric analysis

The representative TG-DTA thermogram of 7,16diacetyl[Ni{ $Me_4(Bzo)_2[14]$ tetraeneN<sub>4</sub>}]-NaY is shown in Fig. 4. The thermal decomposition of all the zeolite encapsulated tetraazamacrocycle complexes occurs in two major steps. The first step corresponds to removal of physically adsorbed



Fig. 3. XRD patterns of zeolite-Y (c), Cu(II)-NaY (b), 7,16-diacetyl  $[Cu\{Bc_0\}_2[14]tetraeneN_4\}]$ -NaY (a).



Fig. 4. TG (blue line) and DTG (red line) thermogram of 7,16-diacetyl[Ni{ $Me_4(Bzo)_2[14]$ -tetraeneN<sub>4</sub>}]-NaY.

water and intrazeolite water molecules and the second step is ascribable to the decomposition of the chelating ligand. In the first step, an endothermic weight loss of ca. 12.1, 16.8, 8.7 and 15.6% in  $[M{Me_4(Bzo)_2[14]tetraeneN_4}]$ -NaY and 7,16diacetvl[M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY (where M = Ni(II)and Cu(II)) take place respectively in the temperature range 90-260 °C. The second step of decomposition starts immediately after the first and in this an exothermic weight loss was observed in several sub-steps in the temperature range 260-900 °C. Weight losses of 13.9, 12.1, 17.3 and 15.0% were observed in [M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and 7,16diacetyl[M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY (where M = Ni(II) and Cu(II)) respectively between 260 and 900 °C. In the second step, the weight loss of zeolite encapsulated metal complexes in each case was in close agreement with the metal content recorded by atomic absorption spectroscopy

## 3.7. Catalytic activity studies

#### 3.7.1. Oxidation of benzyl alcohol

Solvent free catalytic oxidation of benzyl alcohol was studied using H<sub>2</sub>O<sub>2</sub> as oxidant [Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>]-NaY as catalysts. Benzyl alcohol (3.24 g, 30 mmol), 30% H<sub>2</sub>O<sub>2</sub> (5.10 g, 45 mmol) and catalyst (30 mg) were taken in a 50 ml round bottom flask and the reaction mixture was heated at  $75\,^\circ\text{C}$  for 6 h. Generally, benzyl alcohol on oxidation gives benzaldehyde, benzoic acid and benzyl benzoate. However, benzaldehyde was characterized as the major oxidation product in the present case (Scheme 2). Catalysts [Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY showed 27.1 and 29.9% conversion of benzyl alcohol in 6 h, respectively. Selectivity values for benzaldehyde, benzoic acid and benzyl benzoate were found to be 94.1, 1.6 and 4.3% respectively, in the case of [Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and 96.3, 1.2 and 2.5% in the case of 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY, while turn-over frequency values [TOF = moles of substrate converted per mole of metal (in zeolite encapsulated catalyst) per hour] were found to be 110 and 123 h<sup>-1</sup> respectively. The reaction carried out using Cu(II)-NaY as catalyst under the same reaction conditions showed nearly 1.4% conversion of benzyl alcohol. Furthermore in the absence of catalyst, no significant amount of benzaldehyde was produced indicating that H<sub>2</sub>O<sub>2</sub> alone is unable to oxidize benzyl alcohol to benzaldehyde. In order to obtain optimum reaction conditions for maximum conversion of benzyl alcohol, we used catalyst



7,16-diacetyl-[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY as a representative catalyst for further studies.

3.7.1.1. Effect of temperature. The effect of temperature the oxidation of benzyl alcohol using on 7.16diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY as catalyst was investigated at four different temperatures viz. 60, 70, 75 and 80°C, keeping the other parameters fixed: namely benzyl alcohol  $(3.24 \text{ g}, 30 \text{ mmol}), 30\% \text{ H}_2\text{O}_2$  (5.10 g, 45 mmol), catalyst (30 mg) and reaction time (6h). The results are shown in Fig. 5, which reveals that 16.7, 26.9, 29.9 and 30.1% conversion were found corresponding to 60, 70, 75 and 80°C respectively. On increasing the temperature from 75 to 80 °C, only very little improvement (0.2%) in conversion was observed, so that a temperature of 75 °C was considered to be optimum.

3.7.1.2. Effect of catalyst amount. The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. Four different amounts of catalyst viz., 10, 20, 30 and 40 mg were used, keeping with all other reaction parameters fixed: namely temperature (75 °C), benzyl alcohol (3.24 g, 30 mmol) to  $H_2O_2$  (5.10 g, 45 mmol) and reaction time (6 h). The results are shown in Fig. 6, indicating 12.8, 19.7, 29.9 and 30.3% conversion corresponding to 10, 20, 30 and 40 mg catalyst respectively. Lower conversion of benzyl alcohol into benzaldehyde with 10 and 20 mg catalyst may be due to fewer catalytic sites. The maximum percentage conversion was observed with 40 mg catalyst but there was no remarkable difference in the



**Fig. 5.** Effect of temperature on the oxidation of benzyl alcohol, reaction conditions: benzyl alcohol = 30 mmol,  $30\% \text{ H}_2\text{O}_2$  = 45 mmol, catalyst = 30 mg and reaction time = 6 h.



Fig. 6. Effect of amount of catalyst on the oxidation of benzyl alcohol, reaction conditions: benzyl alcohol = 30 mmol,  $H_2O_2$  = 45 mmol, reaction temperature = 75 °C and reaction time = 6 h.

progress of reaction when 30 or 40 mg of catalyst was employed. Therefore, 30 mg amount of catalyst was taken to be optimal.

3.7.1.3. Effect of  $H_2O_2$  concentration. In order to determine the effect of H<sub>2</sub>O<sub>2</sub> on the oxidation of benzyl alcohol to benzaldehyde, we studied the using three different benzyl alcohol: H<sub>2</sub>O<sub>2</sub> molar ratios (1:1, 1:1.5 and 1:2) keeping other parameter fixed: namely catalyst (30 mg), temperature (75 °C) and reaction time (6 h). The results are shown in Fig. 7. A benzyl alcohol to H<sub>2</sub>O<sub>2</sub> molar ratio of 1:1 resulted in 21.4% conversion, and when benzyl alcohol to H<sub>2</sub>O<sub>2</sub> molar ratio was changed to 1:1.5, conversion increased to be nearly 29.9%, keeping all other conditions similar. However, conversion was found to be almost the same at 30.7% when the benzvl alcohol to  $H_2O_2$  molar ratio was further changed to 1:2. The  $H_2O_2$ efficiency  $[H_2O_2 \text{ efficiency } (\%) = (\text{mol of } H_2O_2 \text{ used in product for$ mation/mol of  $H_2O_2$  added) × 100] was found to be 21.6, 67.3 and 51.8%. Therefore, 1:1.5 molar ratio of benzyl alcohol to  $H_2O_2$  was found to be the optimum in terms of conversion as well as  $H_2O_2$ efficiency.

3.7.1.4. Effect of reaction time. The time dependence of catalytic solvent free oxidation of benzyl alcohol was studied by perform-

- 1:1

1:1.5

50

40



**Fig. 7.** Effect of benzyl alcohol:  $H_2O_2$  molar ratios on the oxidation of benzyl alcohol, reaction conditions: benzyl alcohol = 30 mmol, catalyst amount = 30 mg, reaction temperature = 75 °C and reaction time = 6 h.



Scheme 3.

ing the reaction of benzyl alcohol (3.24 g, 30 mmol) with 30% H<sub>2</sub>O<sub>2</sub> (5.10 g, 45 mmol) in the presence of 30 g of catalyst at 75 °C with constant stirring. The percentage of conversion was monitored at different reaction times. It was seen that 29.9% conversion was observed at 6 h; when the reaction was allowed to continue for 20 h, 31.2% conversion was observed.

#### 3.7.2. Oxidation of styrene

Oxidation of styrene was carried out using [Ni{Me<sub>4</sub>(Bzo)<sub>2</sub> [14]tetraeneN<sub>4</sub>}]-NaY and 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY as catalysts in the presence of H<sub>2</sub>O<sub>2</sub>. Oxidation of styrene gives five oxidation products styreneoxide, benzaldehyde benzoic acid, phenylacetaldehyde and 1-phenylethane-1,2-diol (Scheme 3). These products are very common and also have been identified earlier [42-45]. However, styreneoxide and benzaldehyde were characterized as the major oxidation products in the present case. Styrene (1.56 g, 15 mmol), 30% H<sub>2</sub>O<sub>2</sub> (3.52 g, 30 mmol) and catalyst (35 mg) were taken in 10 ml of acetonitrile in a round bottom flask and the reaction mixture was heated at 75 °C. Catalysts 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and [Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY showed 53.5 and 44.2% conversion of styrene in 6h respectively. Turn-over frequencies and product selectivities are shown in Table 3. The highest yield of benzaldehyde might be due to further oxidation of styreneoxide by the nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on styrene oxide, followed by cleavage of the intermediate species hydroxy-hydroperoxistyrene [29]. In order to obtain optimum reaction conditions for maximum conversion of styrene, catalyst 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY was used as a representative catalyst for the following studies.

3.7.2.1. Effect of temperature. In order to determine the optimum temperature for the oxidation of styrene, we investigated the oxidation of styrene using catalyst 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY and 30% H<sub>2</sub>O<sub>2</sub> as oxidant in 10 ml acetonitrile was investigated at four different temperatures 65, 70, 75 and 80 °C, keeping the other parameters fixed, namely styrene (1.56 g, 15 mmol), 30% H<sub>2</sub>O<sub>2</sub> (3.52 g, 30 mmol) and catalyst (35 mg) and reaction time (6 h). The results (Fig. 8) show that 30.9, 45.6, 53.5 and 54.1% conversions were found corresponding to 60, 70, 75 and 80 °C respectively. Only a

Table	e 3
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Product selectivity, % conversion, TOF values of styrene after 6 h reaction time using H<sub>2</sub>O<sub>2</sub> as oxidant.

Catalyst	Conversion (%)	$TOF^{f}(h^{-1})$	Product	Product selectivity (%)				
			So <sup>a</sup>	Bza <sup>b</sup>	Bzac <sup>c</sup>	Phed <sup>d</sup>	Phaa <sup>e</sup>	Others
7,16-diacetyl[Ni{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }]-NaY	53.5	95	18.5	58.2	4.8	5.4	12.3	0.8
[Ni{Me <sub>4</sub> (Bzo) <sub>2</sub> [14]tetraeneN <sub>4</sub> }]-NaY	44.2	78	17.4	61.9	8.0	6.1	5.3	1.3
Cu(II)-NaY	6.2	63	14.4	77.8	1.1	-	7.1	-

<sup>a</sup> Styreneoxide

<sup>b</sup> Benzaldehyde. Benzoic acid.

d

Phenylacetaldehyde.

1-Phenyl-ethane-1.2-diol.

<sup>f</sup> turn-over frequency = mole of styrene converted per mole of metal (in zeolite encapsulated catalyst) per hour.

negligible improvement in conversion was observed on increasing the temperature from 75 to 80 °C. So the temperature of 75 °C was found optimal for the maximum conversion of styrene.

3.7.2.2. Effect of catalyst amount. The amount of catalyst has a considerable effect on the oxidation of styrene. Four different amounts of catalyst viz., 20, 30, 35 and 40 mg were used keeping all other reaction parameters fixed: namely styrene (1.56 g, 15 mmol), 30%H<sub>2</sub>O<sub>2</sub> (3.52 g, 30 mmol), temperature (75 °C) and reaction time (6 h). Fig. 9 shows the results of percent conversion as a function of time, indicating 25.1, 44.9, 53.5 and 54.7% conversions corresponding to 20, 30, 35 and 40 mg of catalyst, respectively. The maximum percentage conversion was observed with 40 mg of catalyst but there was no considerable difference in the styrene conversion



Fig. 8. Effect of temperature on the oxidation of styrene, reaction conditions: styrene = 15 mmol, 30% H<sub>2</sub>O<sub>2</sub> = 30 mmol, CH<sub>3</sub>CN = 10 ml, catalyst = 35 mg and reaction time = 6 h.



Fig. 9. Effect of amount of catalyst on the oxidation of styrene, reaction conditions: styrene = 15 mmol, 30%H2O2 = 30 mmol, CH3CN = 10 ml, reaction temperature =  $75 \circ C$  and reaction time = 6 h.

when 35 and 40 mg of catalyst was used. Therefore, 35 mg amount of catalyst was found to be optimum.

3.7.2.3. Effect of H<sub>2</sub>O<sub>2</sub> concentration. The effect of H<sub>2</sub>O<sub>2</sub> concentration on the oxidation of styrene is illustrated in Fig. 10. It was studied using three different molar ratios of styrene: H<sub>2</sub>O<sub>2</sub> viz., 1:1, 1:2 and 1:3. Other parameters were kept fixed during the reaction: namely styrene (1.56 g, 15 mmol) and catalyst (35 mg) in 10 ml  $CH_3CN$ , temperature (75 °C) and reaction time (6 h). Styrene:  $H_2O_2$ molar ratio 1:1 and 1:2 showed 38.4 and 53.5% conversion respectively. When the styrene to  $H_2O_2$  molar ratio was increased to 1:3, the conversion was found to 52.3% under all other similar conditions. The reason for decreasing % conversion of styrene might be due to dilution of the reaction mixture, since 30% H<sub>2</sub>O<sub>2</sub> has considerable amount of water. Therefore, 1:2 molar ratio of benzyl alcohol to  $H_2O_2$  was found the optimum in terms of conversion as well as cost of H<sub>2</sub>O<sub>2</sub>.

3.7.2.4. Effect of reaction time. The time dependence of the catalytic oxidation of styrene was studied by performing the reaction of styrene (1.56 g, 15 mmol), 30% H<sub>2</sub>O<sub>2</sub> (3.52 g, 30 mmol) and catalyst (35 mg) in 10 ml CH<sub>3</sub>CN at 75 °C for 6 h with constant stirring. The percentage of conversion was monitored at different reaction times. It is seen that 53.5% conversion was observed. When the reaction was allowed to continue for 20 h, 55.0% conversion was observed.

# 3.8. Test for heterogeneity and recycle ability

The recyclability of used encapsulated catalysts has been tested in both the catalytic reactions. The reaction mixture was filtered after a contact time of 6 h. The catalysts were activated by washing with hot acetonitrile and drying at 90 °C in an oven. Each catalyst was used in further catalytic oxidation reactions under similar con-



Fig. 10. Effect of styrene: H<sub>2</sub>O<sub>2</sub> molar ratios on the oxidation of styrene, reaction conditions: styrene = 15 mmol, catalyst amount = 35 mg, CH<sub>3</sub>CN = 10 ml, reaction temperature = 75 °C and reaction time = 6 h.



Fig. 11. Spectral change during titration of 7,16-diacetyl[Ni{ $Me_4(Bzo)_2$  [14]tetraeneN<sub>4</sub>}] with methanolic solution of 30% H<sub>2</sub>O<sub>2</sub>.

ditions. It was found that the conversion was nearly the same as for the first cycle and there was only a minor loss in catalytic activity for the second cycle. In the case of styrene the reaction times increased. This may be due to the blocking of zeolite channels during the reaction. IR spectra of recycled catalysts were found be nearly identical to that of fresh catalysts, pointing to the stability and recyclability of the catalysts. The heterogeneity of the catalysts has been tested in both the catalytic reactions by atomic absorption spectroscopy. The filtrate collected after separating the catalysts were placed in a reaction flask and the reactions were continued after adding fresh H<sub>2</sub>O<sub>2</sub> for another 6 h under conditions similar to those used earlier. The gas chromatographic analysis showed no improvement in conversion after 6 h. The absence of metal in the filtrate of reaction mixtures was confirmed by AAS. This showed that there was no metal leaching during the catalytic reactions, therefore both the reactions were found to be heterogeneous in nature.

#### 3.9. Possible pathway of the catalyzed reactions

To establish the possible path of reactions, a  $10^{-5}$  M solution of neat tetraazamacrocycle complexes 7,16 $diacetyl[M{Me_4(Bzo)_2[14]tetraeneN_4}]$  $\{M = Cu(II),$ Ni(II)} (complexes were first dissolved in minimum amount of chloroform then diluted by methanol) were treated with a methanolic solution of 30% H<sub>2</sub>O<sub>2</sub>. Spectral changes in the electronic spectra of neat complexes were monitored using a UV-vis spectrophotometer. Gradual addition of methanolic solution of 30% H<sub>2</sub>O<sub>2</sub> to the solution of 7,16-diacetyl[Ni{ $Me_4(Bzo)_2[14]$ tetraeneN<sub>4</sub>}] resulted in a decrease in intensity of the 585, 416 and 392 nm peaks while the intensity of the peaks at 335 and 267 nm gradually increased. The spectral changes are shown in Fig. 11. Three isosbestic points were found at 525, 450 and 353 nm. When small drop portions of a methanolic solution of 30% H<sub>2</sub>O<sub>2</sub> were gradually added to  $10^{-5}$  M solution of 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}] spectral changes also occurred as shown in Fig. 12. The intensity of peaks observed at 636, 412, 380 and 314 nm decreased on gradual addition of H<sub>2</sub>O<sub>2</sub> while the intensity of the peaks at 285 and 252 nm increased. An isosbestic point was also found at 302 nm. These changes indicate the interaction of hydrogen peroxide with Cu(II) and Ni(II) metal center.

During catalytic reaction, at least three types of intermediates involving copper–oxygen interaction, viz. side-on Cu<sup>III</sup>-( $\mu$ - $\eta^2$ -peroxo)–Cu<sup>III</sup>, bis( $\mu$ -oxo-Cu<sup>III</sup>) and Cu<sup>III</sup>–O–O–H, have been reported in the literature [45–47]. The encapsulated complexes are expected to have a monomeric structure in each zeolite cavity. This is based on the fact that the size of zeolite cavity constrains the dimensions. Since in each zeolite cavity the monomeric



Fig. 12. Spectral change during titration of 7,16-diacetyl[Cu{Me\_4(Bzo)\_2 [14]tetraeneN\_4}] with methanolic solution of 30% H\_2O\_2.

species of the complexes is present, the formation of [7,16-diacetyl[M{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-(OOH)] {M = Cu(II), Ni(II)} intermediate is expected [45,48,49]. The intermediate species finally transfers oxygen atoms to the substrates to give the products. Thus, the catalytic performance of encapsulated catalyst could be attributed to the facile formation of reversible intermediate species.

# 4. Conclusion

In summary, neat 7,16-diacetyl[M{ $Me_4(Bzo)_2[14]$ tetraeneN<sub>4</sub>}]  $\{M = Cu(II), Ni(II)\}$  have been synthesized and characterized. These square planar complexes have also been encapsulated by the template synthesis method in the super cages of zeolite-Y, and their encapsulation was ensured by different studies. Furthermore, the spectroscopic data suggest that the encapsulated tetraazamacrocycle complex experienced very little distortion in the super cages of zeolite and that chemical ligation to the zeolite surface is minimal. Catalyst 7,16-diacetyl[Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY is a better catalyst for the solvent free oxidation of benzyl alcohol compared to [Cu{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY. Benzaldehyde was found as the major oxidation product along with benzoic acid and benzylbenzoate as minor products. For the oxidation of styrene by  $H_2O_2$  as oxidant, the catalyst 7,16-diacetyl[Ni{Me<sub>4</sub>(Bzo)<sub>2</sub>[14]tetraeneN<sub>4</sub>}]-NaY showed the best performance as compared to  $[Ni{Me_4(Bzo)_2[14]tetraeneN_4}]$ -NaY. Benzaldehyde and styreneoxide were found as major products. All catalysts are stable and reusable. These catalysts do not leach during the reaction, so they can be used as heterogeneous catalysts.

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