Accepted Manuscript

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PII:	\$1381-1169(16)30024-3
DOI:	http://dx.doi.org/doi:10.1016/j.molcata.2016.01.024
Reference:	MOLCAA 9756
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	11-1-2016
Revised date:	21-1-2016
Accepted date:	21-1-2016
Received date: Revised date: Accepted date:	11-1-2016 21-1-2016 21-1-2016

Please cite this article as: Dinesh R.Godhani, Haresh D.Nakum, Digvijaysinh K.Parmar, Jignasu P.Mehta, Nisheeth C.Desai, Tuning of the reaction parameters to optimize allylic oxidation of cyclohexene catalyzed by zeolite-Y entrapped transition metal complexes, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.01.024

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Tuning of the reaction parameters to optimize allylic oxidation of cyclohexene catalyzed by zeolite-Y entrapped transition metal complexes

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Graphical abstract



Highlights

- We have synthesized VO(IV) and/or Fe(II) based neat and their entrapped complexes into the nanopores of zeolite-Y.
- The comparative spectroscopic, thermal, morphological and crystalline properties of these complexes were achieved.
- Their catalytic activities were tested over oxidation of cyclohexene reaction using 30% H₂O₂ as oxidizing agent.
- The reaction parameters were optimized for higher oxidation with higher selectivity towards allylic products.
- Among all catalyst, [VO(hacen)]-Y catalyst shows higher catalytic (TOF, 2963h⁻¹) activity.

ABSTRACT

The synthetic protocols for entrapment of transition metal complexes reported here are to expand the diversity in catalysis made possible by the ability of microporous solid to select reactants, transition states, and products based on their molecular size. Herein, we report a synthetic route for the entrapment of transition metal complexes within the nanopores of zeolite-Y. The complexes of transition metals [M = Fe (II), VO (IV)] with Schiff base ligands that are synthesized by simple condensation of 2-hydroxyacetophenone and/or 2-hydroxy-5-chloroacetophenone with ethylenediamine have been entrapped within nanopores of zeolite-Y by flexible ligand method. These materials have been characterized by various physicochemical and spectroscopic techniques such as ICP-OES, FT-IR, ¹H and ¹³C-NMR, elemental analyzes, and UV-Vis electronic spectral studies, BET, TGA, scanning electron micrographs (SEMs), X-ray diffraction patterns (XRD), conductivity, magnetic susceptibilities as well as AAS. These synthesized catalysts have been utilized as heterogeneous catalysts for liquid phase oxidation of cyclohexene. The reaction parameters have been tuned to optimize higher cyclohexene conversion (%) along with higher selectivity towards the formation of corresponding allylic products. These catalysts were recovered and reused for three times without remarkable loss of activity. Moreover, the intermediate species involved during the catalytic oxidation reaction was synthesized and identified by FTIR and UV-Vis spectroscopy.

Keywords: Zeolite-Y entrapped complexes; Schiff base ligand; oxidation of cyclohexene; optimization of reaction parameters

1. Introduction

Allylic oxidation of olefins is a very chief transformation in synthetic organic chemistry since the products obtained are valuable and resourceful commercial intermediates, and undergo further reactions [1, 2].

Upon oxidation of cyclohexene, which has activated hydrogen at allylic position, it undergoes annoying olefinic oxidation at the double bond in addition to allylic oxidation. It is believed that due to an attack of oxidant at the allylic position as well as at the double bond simultaneously, it lead to the formation two allylic products (2-cyclohexen-1-ol, 2-cyclohexen-1one) and two epoxidation products such as cyclohexene epoxide, and cyclohexane -1,2- diol [3-5]. It has been reported that the type of oxidant used in reaction decides the selectivity of the product. Much better epoxidation occurs at the double bond if hydrogen peroxide, and/or NaOCl, and/or KHSO₅ and/or PhIO are used rather than using bulky tert-butylhydroperoxide (TBHP) as an oxidant, which hinders the attack of oxidant at the double bond of cyclohexene [6-8]. Epoxidation of cyclohexene mainly leads to the formation of cyclohexene epoxide which further transformed to cycloheaxane-1,2-diol in aqueous acidic conditions subsequently [9,10]. While the use of TBHP as an oxidant facilitates the allylic oxidation which leads to the formation of 2cyclohexen-1-one and 2-cylohexen-1-ol [11-13]. Normally, allylic oxidation proceeds via a free radical chain reaction pathway; it generally occurs when the intermediate metallic species are in a low oxidation state [14]. While oxometallic species with higher oxidation state, such as O = Mn^{V} , $O = Ru^{VIII}$ are more likely facilitate olefinic oxidation because these compounds are capable of accepting electron pairs in vacant d-orbital and form stable complexes with organic peroxides having more electrophilic peroxide oxygen atom which readily attacked by an olefinic double bond [15, 16]. Most of the time both mechanisms may occur simultaneously, which leads to the formation of the allylic product along with epoxide products, since tuning in various reaction parameter, may facilitate either allylic oxidation or olefinic oxidation.

However, the homogeneous metal complexes are more active and selective; the catalyst separation from the homogeneous liquid medium is usually troublesome. To tackle this problem, nowadays numerous heterogenization methods of homogeneous catalytic systems are being used to facilitate easy separation of the catalyst and the product(s) such as polymer anchoring [17], polymerization of homogeneous catalyst itself [18], entrapment of metal complex on a solid

support like alumina, silica, or zeolites [19-21], and covalently anchoring to multi-wall carbon nanotubes (MWNTs) [22]. The entrapment of transition metal complex into zeolite-Y is found to be more suitable and ideal because the complex, once formed inside the nanopores of the zeolite-Y, is too large to diffuse out and is not lost into the liquid phase during the reaction.

In present research work, afford have been made to maximize allylic oxidation over olefinic oxidation of cyclohexene using green oxidant hydrogen peroxide (HP), which usually promotes annoying olefinic oxidation. Using various catalysts of Vanadium (IV) and/or Iron (II) complexes with H₂hacen and/or H₂chacen type ligands and/or by tuning the various reaction parameters such as effect of various solvent, ratio of substrate/oxidant, temperature, amount of solvent, reaction time, pH, the amount of catalyst, have been studied to manage higher allylic oxidation. The reaction mechanism was investigated with the all the four neat homogeneous catalysts using Uv-Vis spectroscopy, which support the formation of dimeric metal peroxide species intermediate responsible for oxidation. However, the intermediate is a very active species at reaction temperature and participate in oxidation reactions by transferring one of its oxygen to the cyclohexene.

2. Experimental

2.1 Materials

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications. The compound 2-hydroxyacetophenone, 5-chloro-2-hydroxyacetophenone, and ethylenediamine were purchased from sigma Aldrich Ltd. (India). 70% t-butylhydroperoxide (TBHP), 30% H₂O₂, VOSO₄. 5H₂O and FeSO₄. 7H₂O in extra pure form were purchased from Rankem (India). The Sodium form of zeolite-Y (Si/Al = 5.62) was procured from Hi-media, India.

2.2 Physical methods and analysis

Many various physicochemical methods have been employed to characterize the structure of Schiff base ligand and their neat and zeolite-Y entrapped complexes. The quantitative analysis of Si, Al, Na and transition metal ions of zeolite-Y entrapped complexes was carried out by ICP-OES using a model Perkin Elmer optima 2000 DV. Electronic spectra of Schiff base ligand, their neat complex and VO(IV) and/or Fe(II) entrapped complexes were recorded on "SHIMADZU" UV-2450 spectrophotometer using a quartz cell of 1 cm³ optical path in 10^{-3} M methanol, and/or DMF and/or dilute HF solutions. FTIR (4000-400 cm⁻¹) of Schiff base ligands, and they're neat and entrapped complexes were recorded with KBr on an FTIR-8400S Shimadzu. Thermogravimetric (TG) analysis of ligand, their neat as well as entrapped complexes was carried out in an air atmosphere in the temperature range 30-700 °C using Shimadzu TGA-50 Instrument. The crystallinity of compounds were ensured by powder XRD patterns using Bruker AXS D₈ Advance X-ray powder diffractometer with a CuK α (λ =1.54058) target and movable detector, which scans the intensity of diffracted radiation within the range of 5° to 70° as a function of the angle 20 between the incident and diffracted beams. Scanning electron micrographs (SEMs) of Na-Y, VO(II)-Y, and [VO(hacen)]-Y were carried out using an SEM instrument (model-JSM-5610LV), JEOL to analyze the morphology of the samples. BET surface area and pore volume of Na-Y, M-Y (where M= VO(IV), Fe(II)) and their entrapped complexes were measured by a multipoint BET method using Micromeritics, ASAP 2010 surface area analyzer. Prior to the BET measurements, the samples were de-gasified at 110 °C for 2 h to remove any adsorbed gasses. The magnetic properties of the materials were measured with a magnetic susceptibility balance of models Johnson Matthey and Sherwood. Atomic absorption spectra (AAS) were recorded on a PerkinElmer 4100-1319 Spectrophotometer using a flame approach after acid (HF) dissolution of known amounts of the zeolite material and SiO₂ was also determined by gravimetric analysis. The melting points of the both Schiff bases were determined using a Griffin apparatus and were uncorrected. Proton nuclear magnetic (¹H NMR) resonance spectrum of both Schiff bases was carried out Varian- Gemini (200 MHZ) instrument using CDCl₃ as a solvent. All catalyzed reaction products were analyzed using GC-MS having a BP-5 capillary column ($30m \times 0.25mm \times 0.25m$) 95% silicoxane surface and FID detector. The identities of the products were confirmed by GC-MS model Shimadzu, QP-2012.

2.3 Synthesis section

The synthesis method of the Schiff base, neat transition metal complex, and their respective Zeolite-Y entrapped complex are displayed in scheme 1.

2.3.1 Synthesis of Schiff base ligands

A dropwise addition of a methanolic solution (10 mL) of ethylenediamine (13 mmol, 0.844 mL) into methanolic solution (30 mL) of o-hydroxy acetophenone (26 mmol, 3.85 g) and/or 5-chloro-2-hydroxyacetophenone (26 mmol, 4.50 g) leads to the formation of Schiff base ligand instantly. The progress of the reaction was tested by using thin layer chromatography (TLC) with the suitable solvent system. Once the reaction was completed (3h, 60 °C), the product was filtered, thoroughly washed with methanol, and then dried well. The purified product, H₂ hacen and H₂chacen were crystallized with chloroform and dioxane.

H₂hacen: yellow crystalline, yield 90.90 %, M.P. 198 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 15.94 (2H, s, -OH), δ 2.45 (6H, s, -CH₃), δ 3.94 (4H,s, -H₂C-N), [6.92 (2H, d), 7.50 (2H, d), 6.81 (2H, t), 7.35 (2H, t) for aromatic protons. ¹³C NMR (200 MHz, CDCl₃) δ (ppm) 14.15 (-<u>C</u>H₃ group carbon), ~116.54, ~117.27, ~118.85, ~128.92, ~132.92, ~164.92 ppm corresponding to carbons of the aromatic ring moiety, 175.43 ppm attributed to <u>C</u>=N, 50.27 ppm were assigned N-<u>C</u>H₂ groups. Mass spectrum: The peak at m/z 296 (base peak), other fragments: m/z 161 and 107 were assigned to the loss of C₈H₉ON and C₇H₇O.

H2chacen: yellow amorphous solid, yield 94.93 %, M.P. 233-235 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 16.04 (2H, s, -OH), δ 2.49 (6H, s, -CH₃), δ 4.34 (4H,s, -H₂C-N), [6.90 (2H, d), 7.65 (2H, d), 7.81 (2H, s), for aromatic protons.¹³C NMR (200 MHz, CDCl₃) δ (ppm) 15.45 (-<u>C</u>H₃ group carbon), ~118.54, ~121.27, ~123.85, ~134.92, ~147.92, ~165.92 ppm corresponding to carbons of the aromatic ring moiety, ~173.67 ppm attributed to <u>C</u>=N.~57.37 ppm were assigned N-<u>C</u>H₂ groups.

2.3.2 Synthesis of VO(IV) and Fe(II) based neat transition metal complexes

The procedure for the preparation of VO(IV) and Fe(II) based neat complexes is as follows: 1.13 mmol of Schiff base (H₂hacen or H₂chacen) was dissolved in 15 mL acetone, and then heated to boiling temperature, followed by the dropwise addition of aqueous solution of 1.13 mmol metal salt (VOSO₄·5H₂O and/or FeSO₄· 7H₂O. The pH of the resulting solution was adjusted to 5-6 by dropwise addition of CH₃COONa solution in reaction media. The resultant reaction medium was stirred and refluxed for 4 hours. After cooling, the solid product was separated by filtration and dried in vacuum for overnight at 60 °C.

2.3.3 Synthesis of metal exchanged M-Y [M=Fe(II), VO(IV)]

Metal-exchanged M-Y was prepared by the usual ion-exchange method. As highly concentrate (1 M) metal salt solution causes dealumination in the zeolite framework [23], lower concentrate metal salt solution having a pH range between 4-4.5 were used. Herein, the reaction medium was stirred at 90 °C for 24 h after addition of the 5.0 g of pure Na-Y to the lower concentrated metal salt (0.03 M metal salt, 300 ml, VOSO₄· 5H₂O and/or FeSO₄· 7H₂O) solution having pH 4-4.5. The slurry was filtered and washed with deionized water until the filtrate was free from any free metal ion (filtrate were tested by AAS) on the surface of the zeolite, and dried at 120°C for 12 h.

2.3.4 Synthesis of zeolite-Y entrapped metal complexes

Zeolite-Y entrapped VO(IV) and Fe(II) complexes were prepared by taking 1.0 g of activated M-Y [VO(IV), Fe(II)] successively mixed with an excessive amount of Schiff base ligand (H2hacen or H2chacen) in chloroform (25 mL). It was then refluxed for 16 h with stirring in an oil bath. The filtered solid was treated for Soxhlet extraction with chloroform, methanol, acetone, and acetonitrile to remove uncomplexed ligand and the complex formed on the exterior surface of metal exchanged zeolite-Y. The material then gently stirred for 6 h in an aqueous solution of 0.01 M NaCl to allow the exchange of uncomplexed transition metal ions with sodium ions.

Subsequently, it was washed with deionized water until the filtrate was free from any chloride ions present and then dried overnight at 140 °C.

2.3.5 Catalytic oxidation of Cyclohexene

The catalytic oxidation of cyclohexene by utilizing synthesized catalyst was undertaken in a two-necked 25 mL round bottomed flask. Initially, an arbitrary reaction conditions for the liquid-phase oxidation of cyclohexene were chosen using lesser metal complex loaded entrapped catalyst [VO(hacen)]-Y as a representative catalyst. Subsequently, various reaction parameters were tuned to optimize conversion of cyclohexene along with higher selectivity toward the formation of the allylic product. The progress of the reaction was scrutinized as a function of time by withdrawing small aliquots after certain time intervals and analyzing them quantitatively by gas chromatography technique.

3. Results and Discussion

3.1 Elemental Analysis

The elemental analysis data of both the Schiff base ligand and their respective neat transition complexes are presented in Table 1. The results obtained are in good agreement with those calculated from the suggested formulae and it reveals that each complex is formed in 1:1mole ratio of metal ion and Schiff base ligand. Moreover, the molar conductance of the all synthesized neat complexes is found in a range of 1.00 - 5.00 S cm²mol⁻¹, which reveals that the all the neat complexes are non-ionic in nature and hence has non-electrolytic nature [24]. As shown in Table 2, the Si/Al ratios in VO (IV)-Y, Fe(II)-Y and zeolite- Y entrapped complexes were almost similar as compared to pure Na-Y. This specifies no destruction in the zeolite framework has occurred during ion exchange and entrapment of metal complexes are fewer compared to the metal exchanged VO(IV)-Y, Fe(II)-Y zeolites. This reduction in the metal ion content in the entrapped complexes can be attributed to leaching of some transition metal cation during complex formation inside the nanopores of zeolite-Y. However, the metal to ligand ratio is found to be 1:1

in all neat complexes, the metal ion percentage obtained in zeolite-Y entrapped complexes is slightly higher than that required for 1:1 complexes. Nevertheless, each entrapped catalyst was treated with 0.01 M NaCl to replace the uncomplexed metal ion by Na⁺, a small percentage of uncomplexed transition metal ion still remains trapped in the cage of zeolite-Y that is found to be leached out during (compare entry 5 with 8,9 in table 2) catalytic oxidation of cyclohexene.

3.2 Brunauer, Emmett and Teller (BET) surface area analysis

The BET surface area, Langmuir Surface area, and pore volume data of pure Na-Y and modified zeolite-Y are presented in table 3. The possibility of the destruction of the zeolite-Y framework on ion-exchange can also be ruled out by the fact that only negligible reduction (13-15%) in the surface area, Langmuir Surface area, and pore volume were found upon ion exchange of sodium ion by Fe(II) and/or VO (IV) into the zeolite-Y framework. Furthermore, the data divulge that the surface area, Langmuir surface area, and pore volume are much lower in the case of zeolite-Y entrapped complexes than those of the corresponding metal exchanged zeolite-Y. This reduction in surface area, Langmuir surface area, and pore volume can be attributed to the filling of the zeolite-Y nanopores with transition metal complexes. This adequately indicates the existence of metal complexes inside the nanopores rather than on the external surface of the zeolite-Y. Some workers [25, 26] have reported such lowering in surface area on entrapment earlier.

The BET surface analysis data of the one time used catalyst [VO(hacen)]-Y for oxidation of cyclohexene reveals further lowering in the surface area as compared to fresh catalyst (table 3 entry 5, 8). This might be due to loading of the organic substrate and the product inside the nanopores of zeolite-Y entrapped complexes during the catalytic study. The BET of one time used catalyst [VO(hacen)]-Y taken after dehydrated at various temperature, such as 350°C, 450°C (table 3 entry 9,10) have shown no significance change in surface area, Langmuir surface area, and pore volume suggesting stability of entrapped complex up to 450 °C. Moreover, the unexpected elevation in the surface area, Langmuir surface area, and pore volume of one time used catalyst [VO(hacen)]-Y, which was dehydrated at 550 °C (table 3 entry 11) prior to BET analysis were observed. This might be due to minor breakdown of entrapped metal complex at 550 °C within nanopores of zeolite-Y, which is further supported by TGA.

3.3 X-ray Diffraction (XRD) Study

The powder XRD pattern of the Pure Na-Y, Fe(II)-Y, VO(IV)-Y and their respective entrapped complexes are shown in Figure 1. The XRD patterns of zeolite-Y entrapped complexes are essentially similar to those of pure Na-Y. Nevertheless, there are little changes observed in the relative peak intensities of the 220 and 311 reflections at 10° and 12°, respectively. For pure Na-Y, Fe(II)-Y, and VO(IV)-Y $I_{220} > I_{311}$, however for the entrapped complexes $I_{311} > I_{220}$. This retraction in intensities has been empirically associated with the existence of a large metal complex within the nanopores of zeolite-Y [27-29]. Moreover, no new crystalline pattern appears in the XRD pattern of entrapped complexes, which confirm the preservation of crystalline and the framework of zeolite-Y upon entrapment of the transition metal complexes inside nanopores of zeolite-Y. The XRD pattern of one-time used (for oxidation of cyclohexene) entrapped catalyst [VO(hacen)]-Y were also found to be exactly similar (Figure 1h) as XRD pattern of fresh catalyst [VO(hacen)]-Y. This further signpost that framework of the zeolite-Y does not suffer from any significant structural changes during catalytic study too.

3.4 Scanning Electron Microscopy (SEM) Analysis

Generally, entrapment of metal complex into zeolite-Y is achieved using a flexible ligand (FL) method. In this FL method, the excess amount of Schiff base ligand H₂hacen and/or H₂chacen, which are sufficiently flexible to diffuse into the nanopores of zeolite-Y, were reacted with the pre-exchanged metal ions (Fe(II)-Y and/or VO(IV)-Y) in the nanopores of zeolite-Y to achieve the entrapped complexes. The filtered product may hold the unreacted ligand and the annoying complex formed on the exterior surface of zeolite-Y as impurities. Consequently, these impurities were removed by Soxhlet extraction using various solvents such as chloroform, methanol, acetone, and acetonitrile in order to preclude an intrusion of impurities during the catalytic study. SEMs of Na-Y, VO(IV)-Y, [VO(hacen)]-Y taken before Soxhlet extraction and that of [VO(hacen)]-Y taken after Soxhlet extraction are shown in Figure 2a–d, respectively. As shown in SEM of [VO(hacen)]-Y taken before Soxhlet extraction (Figure 2c), the unreacted ligands and complexes formed on the exterior surface of zeolite-Y are discernable. In the SEM of [VO(hacen)]-Y after soxhlet extraction (Figure 2d), no unreacted ligand and surface complexes could be seen, which indicates the removal of the surface species during soxhlet extraction. The particle boundaries on the exterior surface of zeolite-Y are clearly distinguishable that further

reveals a complete removal of extraneous complexes and unreacted ligand. Furthermore, no new crystalline patterns were observed for the entrapped complexes due to their good distribution in the lattice [30].

3.5 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy is a finer analytical tool to confirm the complexation of the transition metal ions with Schiff base ligand [31, 32]. As shown in figure 3, while comparing the spectra of neat complexes with a respective ligand, $v_{(C=N)}$ band for Schiff base found at ~ 1616 cm⁻¹, which is shifted towards lower wave number (1602- 1580 cm⁻¹) in neat complexes. This provides an evidence of complex formation via coordination of azomethyne nitrogen to a metal center. The weak (due to hydrogen bonding) broadband of $v_{(O-H)}$ present at 3400-3300cm⁻¹ in both Schiff base ligands disappeared in all the neat complexes suggesting coordination of hydroxyl oxygen to a metal center via deprotonation. Moreover, the $v_{(C-O)}$ band for all the neat complexes slightly shifted towards lower wave number compared to that for the free Schiff base ligand, which may be due to the coordination of phenolic oxygen to metal center [33]. A strong broadband in the region 3440–3040 cm^{-1} and a weaker band in the region 620–600 cm^{-1} in neat complexes of iron are ascribed to $v_{(O-H)}$ stretching and wagging vibrations, respectively, which signposted the existence of coordinated water molecules in neat complexes of iron [34]. Binding of metal ions to the ligand through the nitrogen and oxygen atoms is further reinforced by the existence of new bands in the region 570-520cm⁻¹ and 460-420 cm⁻¹due to the v(M-O) and v(M-N) modes, respectively [35]. Both the neat complexes of vanadium exhibit a medium-sharp band around ~ 975 cm⁻¹ due to v(v=0) stretch [36-38].

The FTIR spectra of Na-Y and the modified zeolite-Y (as shown in figure 3) are mainly dominated by the strong zeolitic bands: a broadband in the range $3700-3300 \text{ cm}^{-1}$ and 1635 cm^{-1} due to hydroxyl groups on the surface and lattice water molecules present in zeolite-Y, respectively. As shown in figure 3d-k, the pure Na–Y and modified zeolite-Y material exhibited characteristic bands nearly about ~461, ~680, ~1080 cm⁻¹ attributed to T-O (T= Si, Al) bending mode, symmetric stretching, and antisymmetric vibrations respectively [39]. No shift or broadening of these zeolite-Y vibrations were observed upon entrapment of the complexes, which further divulges that the zeolite-Y framework left over unpretentious upon entrapment of metal complex inside zeolite-Y [40-42]. The bands due to the entrapped metal complexes are

weaker (due to a low concentration of the complexes) and, therefore, could only be observed in the region where the zeolite-Y framework does not absorb (as shown in figure 3f-k) i.e. from 1600–1250 cm⁻¹. The IR bands of entrapped complexes occur at frequencies shifted within 20– 40 cm⁻¹ from those of their respective neat complex (see figure 3 inset). Furthermore, some vicissitudes in band intensities not only confirm the presence of metal complexes in the zeolite-Y but also propose that its structure is almost identical to that of the neat complex with slight distortion in the metal complexes upon entrapment.

As shown in FTIR of entrapped complex, the bands appeared due to of water molecules present in zeolite-Y veneer the weak bands of entrapped metal complex. To ensure this, the FTIR spectrum of the solid samples under vacuum after dehydration is shown in Figure 4. The FTIR spectra of the dehydrated material are found to be much extra strong and no additional peak appeared in the region of 1200–1600 cm⁻¹ (Figure 4). These results confirm the formation of metal complexes inside the zeolite-Y.

3.6 Electronic spectra and magnetic moments

As shown in figure 5a, the electronic spectrum of H₂hacen ligand shows five bands nearly at 390, 320, 284, 272, 256 nm. The first two lower-energy transition are due to $n \rightarrow \pi^*$, and the remaining three high energy bands are due $\pi \rightarrow \pi^*$ transitions occurring in aromatic rings. The electronic spectra of H₂chacen show two bands at 401 and 332 nm due to $n \rightarrow \pi^*$ transition that occurs in azomethyne group. Moreover, H₂chacen ligand display four higher energy bands at 287, 277,263 and 258 nm attributed $\pi \rightarrow \pi^*$ transitions.

It is observed that the vanadium neat complexes of both the ligand give nearly analogous patterns of electronic spectra in methanol. As shown in figure 5c and 5e, both the complex show higher energy bands between 297 - 255 nm, attributed to ligand based $\pi \rightarrow \pi^*$ transition. A blue shift in the one of the higher energy $n \rightarrow \pi^*$ transition of Schiff base was observed in their corresponding vanadium neat complex, which indicate the chelation of the azo-methyne nitrogen to vanadium. The appearance of the new intense *LMCT* transitions in both the vanadium complex at 363-352 nm veiled the second less intense $n \rightarrow \pi^*$ transition, that was clearly seen in the uncomplexed ligand (390 in H₂hacen, 401 in H₂chacen). Moreover, the electronic spectra of

both VO(IV) complex displayed low intensities d-d bands in the range of 869-840, 660-662, and 562-556 nm due to² $b_{2g} \rightarrow e_g$, ${}^{2}b_{2g} \rightarrow {}^{2}b_{1g}$, ${}^{2}b_{2g} \rightarrow {}^{2}a_{1g}$ transition, respectively, characteristic of a square pyramidal geometry around the vanadium ion [43].

In the Fe(II) complexes, four bands are observed virtually at 290, 284, 274, and 261nm due to $\pi \rightarrow \pi^*$ transitions. In addition to these bands, more three bands are observed in both complexes. The bands at 634, 362 and 314 nm in the case of [Fe(hacen)(OH₂)₂]· H₂O and bands at 600, 316, and 296nm in the case of [Fe(chacen)(OH₂)₂]· H₂O are attributable to ${}^5T_{2g} \rightarrow {}^5Eg$ transitions (d-d transition), ligand to metal charge transfer transition (*LMCT*) and $n \rightarrow \pi^*$ transition respectively. The d-d transition is characteristic of the octahedral environment around the iron [44]. The magnetic moment of neat complexes (table 1) of vanadium (IV) and iron (II) complexes were found nearly at 1.61–1.72 and 5.5-5.7 B.M, respectively, which are the characteristic values for mononuclear oxovanadium complex with square pyramidal geometry and mononuclear iron complexes with octahedral geometry surrounded to the central metal ion, respectively [45].

As shown in the figure 5g, pure dehydrated Na-Y shows one intense band at 306 nm and another weak band at 345 nm. Both the transition occurs due to charge transfer for oxygen to aluminum atoms of two different Al–O units present in zeolite-Y [44, 46]. The electronic spectrum of dehydrated Fe(II)–Y shows (Figure 5i) a two bands at 321 and 490nm assigned to ligand to metal charge transfer transition $(t_2g \rightarrow \pi^*)$ and weak *d-d* transition $({}^5T_{2g} \rightarrow {}^5Eg)$, respectively, characteristic of an octahedral configuration around to Fe(II) ions [44]. Additional two bands observed at 341 nm and 306 nm are allied to the zeolite-Y structure. The electronic absorption spectrum (figure 5h) of the dehydrated VO(IV)-Y exhibits six bands at778, 675, 554, 321, 306 and 342 nm. The last two higher energy bands attributed to charge transfer transition (Al←O) in zeolite-Y [46]. The bands observed at 324 is due to charge transfer transition instigated by the transition from oxygen to VO(IV) ion. The first three lower energy bands are assigned to ${}^{2}b_{2g} \rightarrow {}^{2}a_{1g}$, ${}^{2}b_{2g} \rightarrow {}^{2}e_{g}$, and are related to Penta-coordinated VO (IV) ion.

The UV-Vis spectrum of all dehydrated entrapped complex exhibits two bands closely at 306 and 343 nm assigned charge transfer transitions (Al \leftarrow O) in zeolite-Y [44, 46]. The absence of dealumination during synthesis of each entrapped complex was amply confirmed the existence of intense bands at 306 nm due charge transfer transition (Al \leftarrow O) in framework units of zeolite-Y.

As shown in the figure 5k and 5l, the UV-Vis spectrum of both dehydrated VO(IV) entrapped complex shows four higher energy bands closely at 299, 286, 271 and 258nm assigned to $\pi \rightarrow \pi^*$ transitions. The bands at 330-313, 554-550, 709-649,890-883 nm in both VO(IV) entrapped complexes attributed to charge transfer transition (*LMCT*), ${}^{2}b_{2g} \rightarrow {}^{2}a_{1g}$, ${}^{2}b_{2g} \rightarrow {}^{2}b_{g}^{1}$, and ${}^{2}b_{2g} \rightarrow {}^{2}e_{g}$ transitions (*d-d*), characteristic of the square pyramidal geometry of both the complexes.

The electronic spectrum of both the Fe(II) entrapped (Figure 5j, 5m) complex exhibits three higher energy bands below 286 nm due to $\pi \rightarrow \pi^*$ transitions. Moreover, both the entrapped complex displays charge transfer transition (*LMCT*) nearly at 325-322 nm. The two *d*-*d* transition instead of one above 575 nm was observed, this might be due to the distortion in octahedral geometry around the iron (II) ion in zeolite-Y. While comparing electronic spectra of entrapped complex with corresponding neat complex, shifting in the peaks to the lower energy side was observed due to extra splitting of energy levels from the bary center under the influence of the zeolite-Y framework.

3.7 Thermal analysis

The TGA pattern of both the Schiff base H₂hacen and H₂chacen (Figure 6a, 6d) reveals that these ligands decompose in two steps. In the first step, estimated mass loss of 80.11and 76.56% were obtained within the temperature range of 30-300 °C for H₂hacen and H₂chacen, respectively. This first step weight loss may be attributed to major breakdown of the Schiff base ligand. In the secondstep, remaining part of both Schiff base H₂hacen and H₂chacen with an estimated mass loss of 19.89 and 23.44 % were lost due to complete decomposition of Schiff bases as CO, CO₂, NO, NO₂, etc. gasses, respectively.

The TG curve of [VO(hacen)] neat complex found to be (Figure 6b) thermally decomposed in two steps. In [VO(hacen)], first step weight loss about 25.32 % corresponds to the initial breakdown of the neat complex in the range of 27- 400 °C. The second step weight loss of 37.02 % within the temperature range 401-700 °C is credited to the loss of the organic moiety from [VO(hacen)] neat complex. No further weight loss beyond 550 °C were found in the complex, which might be a due fraction of vanadium oxide and carbon residues(37.66 %) remained at the end. Another neat complex [VO(chacen)] decomposes in only one step (Figure 6e) by mass loss of 68.8 % between 27-700 °C owing to lose of the organic moiety and then a leftover fraction of

vanadium oxide and carbon residues (31.20 %).The thermogram of both the Fe(II) complex signifies four stages of decomposition within the temperature range of 27-700 °C. In $[Fe(hacen)(OH_2)_2]$ · H₂O neat complex, the first stage of decomposition(Figure 6c)at 30-120 °C with weight loss of 4.99 %(cal., 4.45%) is corresponding to the loss of one water molecule of hydration. The second step with a weight loss of 6.89 % (cal., 8.90%) at 121-220 °C is attributed to the loss of two coordinated water molecules. The third step at 221- 520°C, with a weight loss of 19.78% owing to the initial breakdown of the complex. The fourth step at 521 -700 °C with a weight loss of 29.85% is referring to the elimination of organic moiety from complex and leaving behind ferric oxide (39.52%) as residue. Neat complex [Fe(chacen)(OH₂)₂]· H₂O shows an almost similar decomposition pattern (Figure 6f) as a former complex of Fe(II). The First and second decomposition steps with a weight loss of 5.11 % (cal. = 3.18%) and 8.40 % (cal., 7.62%) attributed to the loss of one water molecule of hydration and two coordinated water molecules at 27–120 °C, respectively. The third and fourth steps with a weight loss of 51.32% at221-500°C is attributed to the elimination of organic moiety from complex and leaving behind ferric 0.50°C, respectively. The third and fourth steps with a weight loss of 51.32% at221-500°C is attributed to the elimination of organic moiety from complex and leaving behind ferric 0.50°C, respectively. The third and fourth steps with a weight loss of 51.32% at221-500°C is attributed to the elimination of organic moiety from complex and leaving behind Fe₂O₃ as residue (35.01%).

The TGA profile of Na-Y, Fe(II)-Y, and VO(IV)-Y divulges (figure 6g, 6h, 6k) that the thermal decomposition about 11.73, 9.87, and 10.06% were found in the first step at 27-120 °C, respectively. These chief weight losses in these materials may be due the loss of free Intra zeolite water molecules. Furthermore, on increasing the temperature from 120 to 500 °C, considerable weight loss about 5-6 percentage was also observed in each material due to loss of intra zeolite water molecules hydrogen bonded to the oxygen of the zeolite-Y framework. No further weight loss was observed in each material on increasing temperature from 500- 700 °C, leaving back completely dehydrated zeolite-Y material without any damage in its framework. The TGA pattern of zeolite-Y entrapped metal complexes are shown in the figure 6i, 6j, 6l, and 6m, for [Fe(hacen)(OH₂)₂]-Y, [Fe(chacen)(OH₂)₂]-Y, [VO(hacen)]-Y, and [VO(chacen)]-Y, respectively. In addition, to the first and the second step weight loss in each zeolite-Y entrapped metal complex due to the removal of intra zeolite water molecules, each zeolite-Y entrapped complex shows one more decomposition step of about 2-4 % at 500-700 °C. The TG curve of dehydrated [VO(hacen)]-Y shows (Figure 6n) negligible weight loss up to 500 °C and then shows considerable weight loss due to loss of metal complex at 500-700 °C. A lesser weight percentage loss in the third step can be attributed the presence of a small amount of metal complex

entrapped inside the nanopores of zeolite-Y [47]. The decomposition of zeolite-Y entrapped complexes occurred at high temperature as compared to their respective neat complex, which indicates the entrapment metal complex inside the nanopores of zeolite-Y increases their thermal stability due to the shielding effect of zeolite-Y.

4. Catalytic oxidation of cyclohexene

Generally, the oxidation of cyclohexene leads to the formation of 2-cyclohexen-1-ol, 2-cyclohexen-1-one, cyclohexene epoxide, cyclohexane-1, 2-diol [11-13, 48-65]. Herein, reaction conditions for the liquid-phase oxidation of cyclohexene were optimized to manage allylic oxidation over olefinic oxidation of cyclohexene. To afford this, initially, lower metal complexes loaded entrapped catalyst [VO(hacen)]-Y were taken as representative catalyst and reaction condition were optimized one by one as below.

4.1 Influences of various oxidants on cyclohexene oxidation

The effect of different oxidants such as 70% TBHP and/or 30% H_2O_2 on cyclohexene oxidation was carried out by choosing an arbitrary reaction parameter as shown in Table 5. The data presented in table 5 shows that use of hydrogen peroxide as an oxidant gives a higher conversion of cyclohexene (TOF, 716.5) and less number of products than TBHP. Moreover, hydrogen peroxide is a strong oxidant, often more effective, quite cheap, easy to handle and yield water as a byproduct [66]. Hence, hydrogen peroxide is taken as an oxidant throughout for further the catalytic study.

4.2 Influences of various solvent on cyclohexene oxidation

In order to investigate suitable solvent with selectivity towards allylic oxidation products along with the higher conversion of cyclohexene, we studied the oxidation of cyclohexene using [VO(hacen)]-Y as a catalyst and 30 % H₂O₂ as an oxidant in eleven various solvents. As shown in table 6, the solvent with no ability to coordinate with the metal center and lower dielectric constant such as CCl₄, chloroform, and n-hexane, lower conversion (1-7%) of cyclohexene with

higher yield (86-91%) of epoxidation products were obtained. In the polar solvents such as acetonitrile, acetone, dimethyl sulfoxide, ethanol, methanol, dichloromethane-water and non-polar dioxane with the ability to coordinate with metal center high allylic products were obtained. Moreover, coordinating properties of the above solvents with metal center may have produced some short of steric hindrance in the forming metalperoxo intermediate species that are responsible for the epoxidation of cyclohexene, thus mainly allylic products were obtained. Among all these solvent, acetonitrile was found to more appropriate solvent due to their higher ability to yield allylic products (70%) along with considerable cyclohexene conversion (28.66%). Therefore, acetonitrile were chosen for optimization of other reaction parameters in the further catalytic study.

4.3 Influences of various substrate/ oxidant ratios on cyclohexene oxidation

As shown in figure 7, the ratio of cyclohexene/H₂O₂ had a shown remarkable influence on the cyclohexene conversion as well as on the selectivity of the products. The conversion of cyclohexene increase as the cyclohexene/H₂O₂ ratio decrease from 1 to 0.5 with a reduction in the selectivity of allylic products. A further decrease in cyclohexene/H₂O₂ ratio beyond 0.5 reduced conversion of the cyclohexene as well as the selectivity of allylic products. This may be due to excess chemisorption of H₂O₂ rather than cyclohexene on the active sites of catalyst [67]. However, the decreasing of cyclohexene/H₂O₂ ratio from 1 to 0.5 upsurges the cyclohexene conversion from 28.66 to 34.21%, selectivity of allylic products was reduced from 69.9 to 52.7%.Therefore, the cyclohexene/H₂O₂ ratio 1 has been kept as an optimal ratio for further reaction parameter optimization.

4.4 Influences of reaction temperature on cyclohexene oxidation

To find out the effect of reaction temperature, oxidation of cyclohexene was carried out at various temperatures such as 303, 313, 323,333,343, and 353 K. As shown in figure 8, elevation in temperature from 303 to 353 K upsurges the conversion of cyclohexene from 5.6 to 44.38%. Furthermore, the data reveals that lower temperature favors the formation of the cyclohexene oxide (CyOx) and cyclohexene-1,2- diol (Cydiol) whereas higher temperature greatly forces the

reaction to proceed through allylic oxidation resulting in 2-cyclohexen-1-ol (CyOl), 2cyclohexen-1-one (CyOne) as major products. This may be due to less quantity metal peroxo species formation at a higher temperature. Consequently, 353 K has been kept as an optimum reaction temperature for further optimization of reaction parameters.

4.5 Influences of reaction time on oxidation of cyclohexene

As shown in table 7, four reaction times 6, 12, 18, and 24 h were taken into consideration. The presented data reveal that elevation in the reaction time from 6 to 18 h, drastically increase conversion of cyclohexene from 19 to 81.63 % and TOF/h from 92 to 1316 h⁻¹, simultaneously. However, raise in reaction time beyond 18 h upsurge the conversion of cyclohexene, extreme lowering in the TOF was obtained. Thus, reaction time 18 h was taken as an optimal reaction time for optimization of remaining reaction parameters.

4.6 Influences of the solvent amount on oxidation of cyclohexene

The reactions carried out with various quantities of acetonitrile such as 3, 6, 9, and 12 mL divulges that the solvent amount extremely affects the cyclohexene conversion and selectivity. As displayed in figure 9, an increase in acetonitrile amount from 3 to 6 mL slightly increases the cyclohexene conversion from 81.63 to 84.22%. A further increase for acetonitrile causes a large decrease in cyclohexene conversion and selectivity of CyOne. The increase in the amount of acetonitrile prevents the oxidation of formed CyOl and cyclohexene. This may be due to lower concentration of cyclohexene and catalyst at the interface, which results in a decrease in cyclohexene conversion and CyOne selectivity. Consequently, 6 ml of acetonitrile were taken as an optimal amount for optimization of remaining reaction parameters.

4.7 Influence of catalyst amount on oxidation of cyclohexene.

As shown in table 8, the oxidation of cyclohexene was carried out by using six amounts of catalyst (12.5, 25, 37.5, 50, 62.5, and 75 mg) with reaction conditions optimized so far. According to data presented in table 8, it was clear that the 12.5mg of catalyst the led highest

conversion (91.74%) of cyclohexene with a high yield of desired product CyOl and CyOne (97.75%). A gradual drop in cyclohexene conversion was observed with rise in the catalyst amount from 12.5 to 75 mg. This may be attributed to the faster decomposition of H_2O_2 in the presence of an excess catalyst [67]. Additionally, increasing the amount of catalyst decreased the TOF of catalyst and the yield of desired product CyOl and CyOne with more Cydiol. Therefore, 12.5 mg of the catalysts was taken as optimal.

4.8 Cyclohexene oxidation using various catalysts at optimized reaction condition

After optimization of the all reaction parameters (4.1 to 4.7), the catalytic oxidation of cyclohexene was carried out using the neat complexes and their corresponding entrapped complexes as catalysts and 30 % H₂O₂ as an oxidant to assess catalytic efficiency of each catalyst. As presented in table 9, the oxidation of cyclohexene was found to be negligible in the presence of alone Schiff base ligands, pure zeolite-Y, and M(II/IV)-Y, whereas the presence of metal complexes potentially acquired higher conversion of cyclohexene, suggesting itself the chief cause of higher catalytic activity.

As presented in table 9, the neat complexes of VO(IV) and Fe(II) have also shown good activity and higher conversion of cyclohexene as compared to corresponding entrapped complexes. This may be due to the presence of easy accessible catalytic site of the neat complexes for the substrate and oxidant comparative to the deeply buried catalytic site (metal complexes) in the corresponding zeolite-Y entrapped complexes. However, the neat complexes have shown the higher conversion of cyclohexene in the first cycle, were destroyed during the first run due to the continuous degradation of the catalyst, and could not have separated from the reaction medium. The conversion (%) of cyclohexene catalyzed by neat complexes increases in the order: $[VO(chacen)] < [Fe(chacen)(OH_2)_2] \cdot H_2O < [VO(hacen)] < [Fe(hacen)(OH_2)_2] \cdot H_2O$. As shown in table 9, the same trend was observed for the decomposition rate of hydrogen peroxide utilizing various neat complexes, which suggest a directly proportional relationship of cyclohexene conversion with the decomposition rate of hydrogen peroxide.

Zeolite-Y entrapped metal complexes efficiently catalyzed the oxidation of cyclohexene with higher conversion, TOF (h⁻¹) and selectivity towards allylic products. The conversion (%) of cyclohexene catalyzed by zeolite-Y entrapped complexes increases in the order: Na-Y< Fe(II)-Y

< VO(IV)-Y <[Fe(chacen)(OH₂)₂]-Y < [Fe(hacen)(OH₂)₂]-Y <[VO(chacen)]-Y < [VO(hacen)]-Y. However, zeolite-Y based materials containing higher metal ion (%) showed higher decomposition rate of hydrogen peroxide, lower conversion of cyclohexene was obtained. This may be due to higher metal ion concentration in zeolite-Y based material lowersthe effective collision between cyclohexene, oxidant, and metal complex within the zeolite-Y framework, whereas lower concentrations of metal complex effectively react with cyclohexene and oxidant, resulting higher conversion.

It also can be concluded from the results presented in table 9 that the complex having electron withdrawing group (chlorine) substituted at the para position to phenyl ring has shown lower catalytic activity comparable to the complex having no substituent on the ligand. The presence of two electron withdrawing chlorine substituents at para positions of the phenyl group in a complex of H₂chacen Schiff base reduces the electron densities on the ligating atoms of the ligand. It should be noted that the chlorine substituent reduces the electron density at the ortho and para positions with respect to the substituent. Therefore, the "O" atoms in complexes of the H₂chacen Schiff base are likely to be more affected by chlorine groups, whereas in the case of a complex of H₂hacen Schiff base the "O" atoms are the least affected one. Consequently, the metal center of complex bearing H₂hacen is expected to be electron-richer than complexes bearing H₂chacen and it may due to decrease in redox potentials of $M^{(n+1)}/M^{(n)}$, which can easily oxidize complex.

Moreover, in the case of the entrapped catalysts, detection of transition metal ion in the reaction products by AAS indicates leaching of metal ion from the zeolite-Y framework in the first catalytic cycle. It was startling to find that no metal ion leached after the second catalytic cycle. Additionally, upon dropwise addition of H₂O₂ to the decanted liquid of reaction media, no catalytic effect was observed. These facts signpost that the catalytic activities associated with metal complex center entrapped within nanoporoes of zeolite-Y. Catalytic oxidation of cyclohexene using varying homogeneous and/or heterogeneous systems by utilizing various oxidants has been studied earlier by some other groups. As presented in table 10, our catalyst is also being compared with the literate catalysts.

4.9 Influences of acid and base as additives on conversion and selectivity at optimized condition As shown in figure 10, change in the pH by the addition of 2.5 mmol CH₃COONH₄, HCl and CH₃COOH in the reaction medium using [VO(hacen)]-Y as catalyst alters the selectivity and conversion of cyclohexene. The addition of 2.5 mmol HCl or acetic acid to the reaction medium decrease pH from 2 to 1, which obviously increase the conversion of cyclohexene from 91.74 to 97.72 %, but HCl lowers the selectivity of the allylic product whereas acetic acid sustained the selectivity of allylic products. Likewise, the addition of 2.5mmol of ammonium acetate in the reaction medium increases the pH from 2 to 3-6which accelerate decomposition of hydrogen peroxide and increase conversion of cyclohexene up to 100%.

4.10 Possible reaction pathway of catalysts

In order to comprehend the reaction pathway and intermediate species formed during oxidation of the substrates, we examined the progress of the reaction using electronic absorption spectroscopy by treating the 10^{-3} M neat Fe(II) complexes in DMSO with a methanolic solution of H₂O₂. As shown in figure 11a and 11b slight increases in the intensities for the bands appeared below 290 (omitted in the figure) and nearly at 306 nm while the intensity of the band closely at 755 and 340 nm decreased without changing their positions. The intensity of *d*–*d* band was decreased and the band was gradually vanishing with the further addition of H₂O₂. An isosbestic point was found nearly at 308 nm in both Fe(II) complexes clearly indicate the transformation of Fe(II) to Fe(III).

As shown in Fig. 12a, the addition of a methanolic solution of H_2O_2 dropwise to a $10^{-3}M$ methanolic solution of [VO(hacen)] ensued in a slight increase in the intensities for the bands at appeared below 290(omitted in the figure) and at 308nm. While the intensity of the band at 840, 660, 556, and 352nm decreased without changing their positions. The *d*–*d* bands in [VO(hacen)] at 840, 660, and 556, nm were decreased in intensity and the bands were vanishing with the further addition of H₂O₂. As shown in the figure 12b, the dropwise addition of methanolic H₂O₂ to $10^{-3}M$ methanol solution of [VO(chacen)] increase the intensity of bands present below 290 (omitted in the figure) and band at 310 nm. The *d*–*d* band in [VO(chacen)] at 869, 662 and 562 nm were decreased in intensity and the bands were wiped out upon excess addition of H₂O₂. The vanishing of the *d*–*d* band and the appearance of the isosbestic points suggests the conversion of V(IV) complex into aV(V) species [68].

During catalytic reaction using neat VO(IV) complex, at least, two types of intermediates having vanadium-oxygen interaction viz. side-on OV(V)-O-O- VO (V) and OV-O-O-H (vanadium-hydroperoxide) are possible. A separate reaction of 30 % hydrogen peroxide with stoichiometry amount (1:2) of neat [VO(hacen)] (green) at 50 °C for 6 h leads to the formation of the solid brown product. In the FTIR of brown (Figure 13) complex, the absence of $v_{(O-H)}$ band clearly disobeying the formation of the OV-O-O-H species during the reaction, whereas the presence of a strong band at 970 cm⁻¹ attributed to $v_{(V=O)}$, which suggested no involvement of V=O bond in dimerization. Moreover, the appearance of the new band at 565 cm⁻¹which can be attributed to $v_{(V-O)}$, clearly suggesting the dimerization of complex through -O-O- (peroxide), resulted in O=V-O-O-V=O intermediate species. The absence of *d-d* transitions in Uv-Vis spectrum of intermediate species also supports the formation of peroxode species. In entrapped complexes, due to restriction in dimerization executed by zeolite-Y nanopores, the formation of monomeric metal-hydroperoxide in nanopores of zeolite-Y could not be excluded.

The merely tentative mechanism for the oxidation of cyclohexene catalyzed by [VO(hacen)] complexes is shown in Scheme 2. The oxidation of cyclohexene could hypothetically happen via two possible pathways, one is olefinic and other is allylic oxidation. In oxidation, the catalyst interacts with H₂O₂ to form an active dimer O=V-O-O-V=O (II). The activated species II may undergo homolytic cleavage at the reaction temperature (353 K) and undergo oxidative addition to the C–C double bond of cyclohexene to give an intermediate (V). The intermediate (V) undergoes migratory insertion to give cyclohexene epoxide (CyOx) formation through intermediate (VI) and recover I. Furthermore, CyOx species react with H+/H₂O to give Cydiol (V). In the second pathway species(II) attacks at the allylic position of the cyclohexene results in the formation of species (III) which finally form CyOl product. The further attack of species (II) on the CyOl form species (IV) which undergoes further oxidation of CyOl and forms a CyOne with removal of water [69] and regenerates the catalyst I.

Conclusion

The entrapment Fe (II) and VO (IV) Schiff-base complexes within the nanopores of zeolite-Y using the flexible ligand method have been successfully demonstrated. Entrapment of complexes was supported by various physicochemical (XRD, BET, SEM, TGA, ICP-OES) and spectral studies (FTIR, UV) for the well-defined entrapment and distribution of complexes in the

nanopores of the zeolite framework. The catalytic activity of neat and entrapped VO(IV) and Fe(II) complexes were performed over the oxidation of cyclohexene using 30% H₂O₂ as a clean oxidant affording allylic products. The reaction parameters were optimized (25 mmol cyclohexene, 25 mmol H₂O₂, 12.5mg [VO(hacen)]-Y, 6 mL of acetonitrile, 353 K, 18 h) to get maximum allylic oxidation products. It was found that the neat complexes are effective catalysts comparable to their heterogeneous counterpart for oxidation of cyclohexene with H₂O₂.Moreover, effectivity of neat catalyst were found to be related to its capability to decompose hydrogen peroxide. Entrapped complexes, nevertheless, can be recovered and reused without loss of much catalytic activity, making them superior to their homogeneous counterpart.

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Figure Captions

Figure 1 XRD pattern of the fresh [a] Na-Y, [b] Fe(II)-Y, [c] VO(IV)-Y, [d] [Fe(hacen)(OH₂)₂]-Y, [e] [Fe(chacen)(OH₂)₂]-Y, [f] [VO(hacen)]-Y, [g] [VO(chacen)]-Y, and [h] XRD of one time used catalyst [VO(hacen)]-Y.

Figure 2 SE micrograph of (a) Na-Y, (b) VO(IV)-Y, (c) [VO(hacen)]-Y taken before Soxhlet extraction and (d) [VO(hacen)]-Y taken after Soxhlet extraction.

Figure 3 FTIR spectra of [a] Schiff base H₂hacen, Neat complexes [b] $[Fe(hacen)(OH_2)_2] \cdot H_2O$, [c] [VO(hacen)], Zeolite-Y based material [d] Na-Y, [e] Fe(II)-Y, [f] VO(IV)-Y, [g] $[Fe(hacen)(OH_2)_2]$ -Y, [h] [VO(hacen)]-Y, [i] one time used catalyst [VO(hacen)]-Y, [j] $[Fe(chacen)(OH_2)_2]$ -Y, (k) [VO(chacen)]-Y, (l) Schiff base H₂chacen, neat complexes (m) $[Fe(chacen)(OH_2)_2] \cdot H_2O$, and (n) [VO(chacen)]. The inset of FTIR shows the peak values for Zeolite-Y based material in the region of 1800–1000 cm⁻¹.

Figure 4 FTIR spectra of dehydrated zeolite-Y based materials (a) Na-Y, (b) Fe(II)-Y, (c) VO(IV)-Y, (d) [Fe(hacen)(OH₂)₂]-Y, (e) [VO(hacen)]-Y, (f) [Fe(chacen)(OH₂)₂]-Y, and (g) [VO(chacen)]-Y. The inset of FTIR shows the peak values for Zeolite-Y based material in the region of 1700–1100 cm⁻¹.

Figure 5 Electronic spectrum of the [a] H₂hacen, [b] H₂chacen, [c] [VO(hacen)], [d] $[Fe(hacen)(OH_2)_2] \cdot H_2O$, [e] [VO(chacen)], [f] $[Fe(chacen)(OH_2)_2] \cdot H_2O$, [g] Na-Y, [h] VO(IV)-Y, [i] Fe(II)-Y, [j] $[Fe(hacen)(OH_2)_2]$ -Y, [k] [VO(chacen)]-Y, [l] [VO(hacen)]-Y, [m] $[Fe(chacen)(OH_2)_2]$ -Y.

Figure 6 TGA pattern of the [a] H₂hacen, [b] [VO(hacen)], [c] $[Fe(hacen)(OH_2)_2] \cdot H_2O$, [d] H₂chacen, [e] [VO(chacen)], [f] $[Fe(chacen)(OH_2)_2] \cdot H_2O$, [g] Na-Y, [h] Fe(II)-Y, [i] $[Fe(hacen)(OH_2)_2]$ -Y, [j] $[Fe(chacen)(OH_2)_2]$ -Y, [k] VO(IV)-Y, [l] [VO(hacen)]-Y, [m] [VO(chacen)]-Y, [n] dehydrated [VO(hacen)]-Y.

Figure 7 Influences of cyclohexene/H₂O₂ ratio on cyclohexene oxidation and selectivity of products.

Reaction condition: 25 mmol cyclohexene, 25, 50, 75 and 100 mmol 30% H_2O_2 , 25 mg [VO(hacen)]-Y, 3 mL of acetonitrile, 343 K, 12 h.

Figure 8Influences of the reaction temperature on the oxidation of cyclohexene.

Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 25 mg [VO(hacen)]-Y, 3 mL of acetonitrile, various temperature (K), 12 h.

Figure 9Influences of the amount of acetonitrile (solvent) on oxidation of cyclohexene.

Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 25 mg [VO(hacen)]-Y, Different amount (mL) of acetonitrile, 353 K, 18h.

Figure 10Influences of acid and base as an additive on oxidation of cyclohexene.

Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 12.5 mg [VO(hacen)]-Y, 6 mL of acetonitrile, 353 K, 18 h, 2.5 mmol of additives.

Figure 11 UV–Visible spectral studies (a) neat $[Fe(hacen)(OH_2)] \cdot H_2O$ and (b) $[Fe(hacen)(OH_2)] \cdot H_2O$ of after the sequential dropwise addition of a methanolic solution of H_2O_2 .

Figure 12 UV–Visible spectral studies of (a) neat [VO(hacen)] and (b) [VO(chacen)] after the sequential dropwise addition of a methanolic solution of H_2O_2 .

Scheme 1 Schematic diagram of synthesis pathway of Schiff bases, neat complexes, metal exchanged Na-Y and zeolite-Y entrapped complexes.

Scheme 2 The merely tentative reaction mechanism for oxidation of cyclohexene with H_2O_2 catalyzed by [VO(hacen)].







Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8











Figure 11



Figure 12



Figure 13



Scheme 1



Scheme 2

Table 1 Chemical composition, physical properties, conductivity, the magnetic moment of Schiff base ligands and their respective neat metal complexes.

	Elementa	l analysis									µeff
Catalyst	%Found	(Calculate	d)				Ratio	Yield	M.P	Molar	(B.M)
							(%)	(%)	(°C)	Conductivity ^b	
	С	Н	N	M ^a	0	Cl	C/N			$(S \text{ cm}^2 \text{ mol}^{-1})$	
H ₂ hacen	72.11	6.99	9.31	-	11.59	-	7.74	90.90	198	-	С
	(72.95)	(6.80)	(9.45)		(10.80)		(7.72)				
H ₂ hcacen	59.09	5.01	7.66	-	8.83	19.41	7.71	94.93	~233	-	С
	(59.19)	(4.97)	(7.67)		(8.76)	(19.41)	(7.72)				
[Fe(hacen)(OH ₂) ₂]· H ₂ O	55.67	6.02	7.19	14.21	16.91	-	7.74	80.09	>300	4.00	5.62
	(53.48)	(5.98)	(6.93)	(13.81)	(19.80)		(7.72)				
[VO(hacen)]	59.03	5.48	7.61	13.10	14.78	-	7.75	91.11	>300	1.53	1.62
	(59.84)	(5.02)	(7.75)	(14.10)	(13.28)		(7.72)				
[Fe(chacen)(OH ₂) ₂]· H ₂ O	47.32	4.58	6.12	12.29	14.11	15.58	7.73	95.56	>300	4.54	5.69
	(45.70)	(4.69)	(5.92)	(11.80)	(16.91)	(14.99)	(7.72)				
[VO(chacen)]	50.32	3.98	7.40	11.30	14.77	12.23	7.70	60.33	>300	2.01	1.71
	(50.26)	(3.75)	(6.51)	(11.84)	(11.16)	(16.48)	(7.72)				

^{*a*}Respective transition metal Fe(II) or V(IV).

^bConductivity of the neat metal complex was measured using DMSO as solvent at 30 °C.

^c Diamagnetic

Entry	Catalyst	ICP-O	ES Eleme	ental analy	ysis (%)			Percentag	e Ratio	Unit cell formula
No.		С	N	Na	М	Si	Al	Si/Al	C/N	-
1	Na-Y	-	-	4.992	-	32.936	6.054	5.62	-	$Na_{30}[(AlO_2)_{30}(SiO_2)_{162}]$
2	Fe(II)-Y	-	-	4.289	1.081	33.757	6.006	5.62	-	$Na_{25.14}Fe_{2.43}[(AlO_2)_{30}(SiO_2)_{162}]$
3	VO(IV)-Y	-	-	4.467	0.710	33.749	6.004	5.62	-	$Na_{26.20}V_{1.90}[(AlO_2)_{30}(SiO_2)_{162}]$
4	[Fe(hacen)(OH ₂) ₂]-Y	3.161	0.401	4.300	0.898	33.289	5.920	5.62	7.90	$Na_{25.60}[Fe_{2.20}(hacen)_{1.99}(AlO_2)_{30}(SiO_2)_{162}]$
5	[VO(hacen)]-Y	0.679	0.088	4.731	0.175	34.875	6.204	5.62	7.71	$Na_{29.10}[V_{0.45}(hacen)_{0.41}(AlO_2)_{30}(SiO_2)_{162}]$
6	[Fe(chacen)(OH ₂) ₂]-Y	2.930	0.382	4.329	0.937	33.058	5.881	5.62	7.71	$Na_{25.38}[Fe_{2.31}(chacen)_{1.87}(AlO_2)_{30}(SiO_2)_{162}]$
7	[VO(chacen)]-Y	1.046	0.135	4.555	0.379	34.945	6.216	5.62	7.52	$Na_{28.06}[V_{0.97}(chacen)_{0.63}(AlO_2)_{30}(SiO_2)_{162}]$
8	[VO(hacen)]-Y ^a	0.741	0.083	4.467	0.169	32.924	5.857	5.62	8.92	$Na_{29.10}[V_{0.43}(hacen)_{0.41}(AlO_2)_{30}(SiO_2)_{162}]$
9	[VO(hacen)]-Y ^b	0.707	0.091	5.341	0.169	36.290	6.456	5.62	7.71	$Na_{29.10}[V_{0.43}(hacen)_{0.41}(AlO_2)_{30}(SiO_2)_{162}]$
10	[VO(hacen)]-Y ^c	0.709	0.0918	5.344	0.169	36.395	6.474	5.62	7.71	$Na_{29.10}[V_{0.43}(hacen)_{0.41}(AlO_2)_{30}(SiO_2)_{162}]$

Table 2 ICP-OES analysis data of pure Zeolite-Y (Na-Y) and modified Zeolite-Y material with their possible unit cell formulae.

^a Analyzed after one catalytic cycle without dehydrated.

^b Analyzed after one catalytic cycle after dehydrated overnight at 250 °C.

^c Analyzed after second catalytic cycle and dehydrated overnight at 250 °C.

Entry	Catalyst	Surface area	Pore volume	Langmuir Surface	Loss in pore
No.		(m ² /g)	(cm^2/g)	area (m²/g)	volume (%)
1	Na-Y	539.09	0.3275	861.29	-
2	Fe(II)-Y	465.61	0.2800	705.02	13.63
3	VO(IV)-Y	450.60	0.2539	682.22	16.41
4	[Fe(hacen)(OH ₂) ₂]-Y	265.42	0.1612	401.89	42.99
5	[VO(hacen)]-Y	099.15	0.0267	128.56	77.99
6	[Fe(chacen)(OH ₂) ₂]-Y	238.09	0.1446	360.51	48.86
7	[VO(chacen)]-Y	127.34	0.0341	162.30	71.73
8	[VO(hacen)]-Y ^b	084.27	0.0226	109.26	81.29
9	[VO(hacen)]-Y ^c	100.10	0.0269	129.79	77.78
10	[VO(hacen)]-Y ^d	102.90	0.0277	133.42	77.16
11	[VO(hacen)]-Y ^e	323.00	0.1975	561.04	28.31

Table 3 BET^{*a*} surface analysis of pure Zeolite-Y and modified Zeolite-Y material.

^a Before analysis , all samples (1-7) were de-gasified at 110 °C for 2 h to remove any adsorbed gases. ^b Analyzed after one catalytic cycle and de-gasified at 110 °C for 2 h to remove any adsorbed gases. ^c Analyzed after one catalytic cycle and dehydrated overnight at 350 °C. ^d Analyzed after one catalytic cycle and dehydrated overnight at 450 °C. ^e Analyzed after one catalytic cycle and dehydrated overnight at 550 °C.

 Table 4 UV-Vis spectrum of Schiff base ligands, neat complexes, zeolite-Y and modified Zeolite-Y material.

Catalyst	Electronic transition (nm)					
	$\pi \rightarrow \pi^* \text{ (strong)}$	$n \rightarrow \pi^*$	LMCT (strong)	d-d transition (weak)		
		(weak)				
H ₂ hacen	256, 272, 284	320, 390	-	-		
H ₂ hcacen	258, 263, 277, 287	332, 401	-	-		
[Fe(hacen)(OH ₂) ₂] · H ₂ O	261, 274, 287, 292	314	363	634		
[VO(hacen)]	272, 282, 297	308	352	556, 660, 840		
[Fe(chacen)(OH ₂) ₂]· H ₂ O	261, 273, 284, 290	296	316	600		
[VO(chacen)]	255, 262, 275, 289	310	363	562, 662, 869		
Na-Y	-	-	306, 345	-		
Fe(II)-Y	-	-	321, 306, 341	490		
VO(IV)-Y	-	-	324, 306, 342	554, 675, 778		
[Fe(hacen)(OH ₂) ₂]-Y	261, 275, 286	312	325, 306, 343	640, 665		
[VO(hacen)]-Y	261, 273, 285, 298	-	313, 307, 343	550, 709, 883		
[Fe(chacen)(OH ₂) ₂]-Y	254, 275, 284	-	322, 305, 343	575, 670		
[VO(chacen)]-Y	256, 270, 287, 299	318	330, 308, 346	554, 649, 890		

Oxidant	Conversion ^a	Selectivity	Selectivity (%)						
	(%)	CyOl ^e	CyOne ^f	CyOx ^g	Cydiol ^h	Cytbp ⁱ	_		
30% H ₂ O ₂ ^c	28.66	30.11	39.78	26.31	03.80	-	716.5		
70 % TBHP ^d	27.51	18.32	20.57	36.47	09.79	14.82	687.7		

Table 5 Influences of various oxidants on cyclohexene oxidation.

^a Conversion refers to fraction of starting material (cyclohexene)used up in the reaction. ^b Moles of cyclohexene converted per mole of active metal ion per hour. ^c Hydrogen peroxide as oxidant. ^d t-butyl hydroperoxide as oxidant. ^e 2-Cyclohexen-1-ol. ^f 2-Cyclohexen-1-one. ^g Cyclohexene oxide (1,2-epoxycyclohexane). ^h Cyclohexene-1,2-diol. ⁱ Cyclohexene-3-(<u>tert-butyl</u>)peroxide. Reaction condition: 25 mmol cyclohexene, 25 mmol oxidant, 25 mg [VO(hacen)]-Y, 3 mL of Acetonitrile, 343 K, 12 h.

Solvent	Conversion ^a	Selectivity (%)			
	(%)	CyOl	CyOne	CyOx	Cydiol
Nil	11.23	60.60	24.24	-	15.16
Water	09.66	44.30	28.85	-	26.28
Methanol	16.23	50.98	36.87	-	12.15
Ethanol	13.56	39.27	36.03	-	24.70
Acetone	34.18	26.47	24.35	03.65	45.53
DMF ^b	22.43	30.10	26.82	-	43.08
Acetonitrile	28.66	30.11	39.78	26.31	03.80
DCE ^c	03.85	42.23	51.94	02.42	03.41
n-hexane	01.22	-	10.55	-	89.45
Dioxane	06.10	39.40	34.02	-	26.58
Chloroform	07.12	-	13.47	-	86.53
CCl ₄	04.78	-	08.12		91.88

Table 6 Influences of various solvents on oxidation of cyclohexene and selectivity of the product.

^a Conversion refers to fraction of starting material (cyclohexene) used up in the reaction.

^b Dimethylformamide, ^c 1,2-Dichloroethane.

Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 25 mg [VO(hacen)]-Y, 3 mL of solvent, 343 K, 12 h.

Reaction	Conversion ^a	Selectivity (%	Selectivity (%)					
time (h)	(%)	CyOl	CyOne	CyOx	Cydiol			
6	19.00	06.82	93.18	-	-	92.28		
12	44.38	08.62	91.38	-	-	1077		
18	81.63	46.12	52.36	01.52	-	1316		
24	96.16	43.72	49.18	-	07.10	1166		

 Table 7 Influences of reaction time on the oxidation of cyclohexene.

^a Conversion refers to fraction of starting material (cyclohexene)consumed in the reaction. ^b Moles of cyclohexene converted per mole of active metal ion per hour. Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 25 mg [VO(hacen)]-Y, 3 mL of acetonitrile, 353 K, various reaction time (h).

Amount of	Conversion ^a	Selectivity	Selectivity (%)					
catalyst (mg)	(%)	CyOl	CyOne	CyOx	Cydiol	_		
12.5	91.74	47.47	50.28	-	2.25	2966.1		
25	84.22	53.67	46.33	-	-	1362.5		
37.5	66.51	64.90	35.10	-	-	716.78		
50	50.98	91.40	08.60	-	-	428.69		
62.5	36.00	79.16	15.70	04.83	-	232.86		
75	16.29	82.87	10.29	06.84	-	87.948		

Table 8 Influences of catalyst amount on the oxidation of cyclohexene.

^a Conversion refers to fraction of starting material (cyclohexene)consumed in the reaction. ^b Moles of cyclohexene converted per mole of active metal ion per hour. Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H_2O_2 , Different amount (mg) of [VO(hacen)]-Y, 6 mL of acetonitrile, 353 K, 18 h.

Catalyst	Conversion	Selecti	vity (%)			Metal	TOF/h ^b	Decomposition
	^a (%)	CyOl	CyOne	CyOx	Cydiol	- atom (mmol) in catalyst ^c		rate of 30% H ₂ O ₂ (mmol/h) ^d
Nil	03.60	28.90	09.18	45.66	16.26	-	-	0.043
H ₂ hacen	04.70	27.85	23.23	41.43	07.49	-	-	0.053
H ₂ chacen	03.99	31.48	13.67	49.24	06.61	-	-	0.051
Na-Y	07.40	13.71	15.76	61.65	08.88	-	-	0.061
Fe(II)-Y	14.67	32.72	37.70	15.70	13.88	0.00241	84.19	0.891
VO(IV)-Y	19.30	21.40	50.16	18.34	10.10	0.00174	153.9	0.491
[Fe(hacen)(OH ₂) ₂] · H ₂ O	97.82	35.88	30.87	-	33.25	0.03180	42.70	2.083
[VO(hacen)]	95.74	48.47	49.28	-	02.25	0.03214	41.36	1.880
[Fe(chacen)(OH ₂) ₂] · H ₂ O	80.00	38.00	39.58	-	22.42	0.02750	40.68	1.790
[VO(chacen)]	77.78	49.55	48.46	0.050	01.94	0.02772	38.94	1.540
[Fe(hacen)(OH ₂) ₂]-Y	63.69	38.40	52.53	05.57	03.50	0.00201	440.0	0.810
[VO(hacen)]-Y	91.74	47.47	50.28	-	02.25	0.00042	2966	0.285
[Fe(chacen)(OH ₂) ₂]-Y	58.72	42.17	52.93	0.490	04.41	0.00209	388.0	0.864
[VO(chacen)]-Y	72.09	45.35	47.22	-	07.43	0.00092	1078	0.311
[VO(hacen)]-Y ^e	88.49	47.57	50.15	-	02.28	0.00041	2963	-
[VO(hacen)]-Y ^f	88.20	46.21	51.28	-	02.51	0.00041	2954	-
[VO(hacen)]-Y ^g	87.90	47.11	50.44	-	02.45	0.00041	2944	-

Table 9 Conversion and Selectivity for the cyclohexene oxidation catalyzed by the synthesized catalyst at optimized reaction parameters.

^a Conversion refers to fraction of starting material (cyclohexene) consumed in the reaction. ^b Moles of cyclohexene converted per mole of active metal ion per hour. ^c Amount of metal atom in mmol present per 12.5 mg of catalyst. ^d Reaction was carried out separately, reaction condition: 25 mmol of 30% H₂O₂, 12.5 mg catalyst, 353 K, 1h. Decomposition rate was measured by using KMnO₄ and/Or standard iodimetric method. ^e First reuse of catalyst. ^f second reuse of catalyst. ^g third reuse of catalyst. Reaction condition: 25 mmol cyclohexene, 25 mmol 30% H₂O₂, 12.5 mg Catalyst, 6 mL of acetonitrile, 353 K, 18 h.

 Table 10 Comparison of literature catalysts and our catalyst system for oxidation of cyclohexene.

CyOl: 2-Cylohexen-1-ol, CyOne: 2-Cyclohexen-1-one, CyOx: Cyclohexene oxide, Cydiol: Cyclohexane-1,2-diol, Dcyeth: di-2-cyclohexenylether.

Catalyst	Oxidant	Conversion	Selectivity	References
		(%)	(%)	
[VO(L1)(acac)]	H_2O_2	87.2	CyOl (46.0)	48
FeTMC-Y	PhIO	40.0	CyOx (50.8)	49
[Mn(bpch)]-Y	H_2O_2	97.0	Cydiol (49)	50
Cu–NaY	TBHP	45.7	Dcyeth (71.20)	51
[Co(PAN)Cl]	TBHP	59.0	CyOx (65)	52
[Mn(Bzo2[12]aneN4)] ²⁺ –NaY	TBHP	90.4	Dcyeth (81.72)	53
$[Mn(H_4C_6N_6S_2)]-NaY$	TBHP	90.3	CyOne (87.5)	12
[Ni((C ₆ H ₅) ₂ [12]1,3-dieneN ₂ O ₂)] ²⁺ @K10	O ₂	70.3	CyOne (65.4)	54
[Ni(Bzo2[14]aneN4)](ClO4)2	O_2	53.8	CyOne (61.5)	13
[Mn(sal-1,3-phen)]-NaY	TBHP	85.1	CyOne (86.3)	11
Cu-Sal	O ₂	33.6	CyOne (55)	55
[MoO ₂ HL(HOCH ₃)]	TBHP	100.0	CyOl (87)	56
[Fe ₃ O ₄ @SiO ₂ /[MoO ₂ L(HOCH ₃)	TBHP	82.0	CyOl (69)	56
[Mn(THPP)OAc]@MWCNT	H_2O_2	24.0	CyOx(24)	57
$[Mn_3(BDC)_3(DMF)_4]_n$	TBHP	66.0	CYOx(<1)	58
Calcined (Cr)MCM-48	TBHP	67.4	CyOne(82.9)	59
[Mn(salpnMe ₂)]–Al ₂ O ₃	TBHP	77.9	CyOne (77.9)	60
$[Ni((C_6H_5)_2[12]_{1,3}-dieneN_2O_2)]^{2+}-NaY$	O_2	67.5	CyOl (68.2)	61
$[Cu((C_6H_5)_2[13]_{1,4}-dieneN_2O_2)]^{2+}@K10$	TBHP	56.3	CyOx(50.6)	62
${[Ni([16]aneN_5)]_2R}(ClO_4)_4$	O_2	53.9	CyOl (72.5)	63
[CuL]-NaY	H_2O_2	42.9	CyOne (82.5)	64
[Ni([H]2-N4)]2þ–NaY	O_2	70.8	CyOl (73.8)	65
[VO(hacen)]-Y	H_2O_2	100	CyOl+CyOne	This study

CyOl: 2-Cylohexen-1-ol, CyOne: 2-Cyclohexen-1-one, CyOx: Cyclohexene oxide, Cydiol: Cyclohexane-1,2-diol, Dcyeth: di-2-cyclohexenylether.

References in bold letters indicate addition of references as suggested by learned reviewers.