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Zeolite Y encaged Ru(III) and Fe(III) complexes for oxidation of styrene, cyclohexene, limonene, and  $\alpha$ -pinene: an eye-catching impact of H<sub>2</sub>SO<sub>4</sub> on product selectivity

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#### **Graphical Abstract**



### Highlights

- A Ru(III) and Fe(III) complexes are successfully encapsulated and is buttressed by ICP-OES, BET, FTIR, Uv-Vis and TG analysis.
- The addition of H<sub>2</sub>SO<sub>4</sub> yields 100% conversion with epoxidation products mainy, whereas, lower conversion of substrates with high selectivity of allylic products is obtained in the absence of H<sub>2</sub>SO<sub>4</sub>.
- The absence of metal ion leaching from zeolite Y during catalytic study is reinforced by AAS and ICP-AES.

### ABSTRACT

A novel Ru(III) and Fe(III) complexes of ligands 1 and/or 2 (where 1=2.2'-((1E.1'E)-((azanediylbis(ethane-2,1-diyl))bis(azanylylidene))bis(methanylylidene))diphenol and 2= 2,2'-((1E,1'E)-((azanediylbis(ethane-2,1-diyl))bis(azanylylidene))bis(methanylylidene)) bis(4-nitrophenol)} have been synthesized as 'neat' and zeolite Y encapsulated complexes. These catalysts are characterized by various analytical tools such as FTIR, UV–Vis, elemental analysis, ICP-AES, molar conductivity, <sup>1</sup>H- and <sup>13</sup>C-NMR, TGA, SEM, AAS, BET, magnetic susceptibility and powder XRD to endorse the complex formation, absence of peripheral redundant ligands and complexes, conservation of zeolite Y morphology and crystallinity, and the encapsulation of complexes without devastation in the zeolite Y framework. Out of these synthesized catalysts, 5Y is found to be a potent candidate for styrene (Conv. 76.1%, TOF: 2130 h<sup>-1</sup>), cyclohexene (Conv. 84.4%, TOF: 2351 h<sup>-1</sup>), limonene (Conv. 81.6%, TOF: 2273 h<sup>-1</sup>), and α-pinene (Conv. 72.6 %, TOF: 2023 h<sup>-1</sup>) oxidation with high selectivity of respective allylic products excluding the styrene oxidation, which undergoes epoxidation only. The addition of H<sub>2</sub>SO<sub>4</sub> in an identical reaction catalyzed by 5Y not only surge the conversion up to 100 % in a short time span with high TOF but also increase the selectivity of respective epoxidation products. This switchover in the selectivities could be credited to the presence of H<sub>2</sub>SO<sub>4</sub> that facilitates the heterolytic –O–O– bond cleavage of metal hydroperoxide and stimulates the epoxidation over allylic oxidation. Furthermore, the results establish that the heterogeneous systems are effortlessly recovered and reused without ample drop in the activity and selectivity.

Keywords: Metal complex; Oxidation; Metal-oxo intermediate; H<sub>2</sub>SO<sub>4</sub>; Selectivity

#### 1. Introduction

Transition metal-catalyzed allylic C–H oxidation is facilitating approach for sustainable synthesis and has grown remarkable attention due to its ability to simplify the transformation of olefins having an allylic C–H bond to the oxy-functionalized derivatives [1, 2]. Applications of oxyfunctionalization range from the synthesis of the natural product, perfume, pharmaceutical, plasticizers, coating materials and drug discovery to the synthesis of fine and commodity chemicals [3, 4]. Although a number of transition metal-catalyzed oxyfunctionalization reactions are available at present [5-7], the use of precious metal complexes such as Rh, Ru, Ir and Pt are relatively less studied and are preferred extensively due to its high selectivity towards the formation desired products with the lower amount of by-products [8]. In such oxidation, a high-valent metal–oxo active species engendered in situ with an oxidant can act as effective oxidizing agents and facilitate allylic C–H oxidation of substrate with trivial provoking epoxidation [9, 10].

The homogeneous neat metal complexes are a lot more active and more selective due to presence of easily accessible active sites in it; however, apart from the demerits of trouble in the separation and recycling of these catalysts, the contamination of toxic metal due to homogeneous neat complex degradation in the products is an acute matter, especially for the synthesis of biologically active intermediates and products. In this context heterogenization of homogeneous catalyst seek utmost attention as it confines the leaching of toxic metal ions in the products, easily recyclable, highly stable, can operate at severe conditions and can be reused over and over again [11-21].

For heterogenization, zeolites are superlative supports and incisive choice for the metal complex encapsulations [22-32]. Once an active metal complex formed inside the ordered supercages of zeolite Y, it impedes the diffusion of metal complexes from the supercages, which minimize the possibility of toxic metal ion leaching into the products.

In these architectures, zeolite Y obliges as a substitute scaffold for the metal complexes and provides a controlled steric environment, where the reaction can proceed [33].

The present article focus on synthesis, characterization and catalytic aspects of zeolite Y encapsulated Fe(III) and costly Ru(III) complexes bearing 1 and/or 2 ligands along with the respective neat metal complexes (homogeneous catalysts). The catalytic potential of these novel hybrid catalysts and neat complexes was studied over the selective oxidation of limonene, cyclohexene, styrene, and α-pinene with 30% H<sub>2</sub>O<sub>2</sub> as an oxygen donor. Moreover, the identical reaction catalyzed by 5Y was carried out using 2.5 mmol H<sub>2</sub>SO<sub>4</sub> as an additive to investigate the change in % conversion and selectivity of products. The detailed mechanistic study using UV-Vis and the changes observed while using H<sub>2</sub>SO<sub>4</sub> during the reaction clearly point out that M(V)=O and M(IV)=O species may involve during the oxidation, which are formed by heterolytic and/or homolytic -O-O bond cleavage of sluggish metal-hydroperoxide, respectively.

#### 2. Experimental section

#### 2.1 Materials

All chemicals such as 2-hydroxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, diethylenetriamine, R-(+)-limonene, styrene, α-pinene, cyclohexene, RuCl<sub>3</sub>·3H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and zeolite Y (Si/Al: 5.62) were purchased from Aldrich, Rankem (India) and Hi-media with the maximum purity available and used as received unless otherwise specified.

#### 2.2 Physical methods and analysis

Many analytical tools have been used to characterize the synthesized materials or complexes and ligands. Before the analysis, zeolite Y based materials were dehydrated at 100 °C for 3 h to confiscate the maximum amount of physically and chemisorbed water molecules. The quantitative analysis of Si, Al, Na, Fe(III), and Ru(III) was carried out by ICP-AES using a model Perkin Elmer Optima 2000 DV. Electronic spectra were carried out on "SHIMADZU" UV-2450 spectrophotometer using a quartz cell of 1 cm<sup>3</sup> optical path in 10<sup>-3</sup> M methanol, and/or dilute HF solutions. FTIR (4000-400 cm<sup>-1</sup>) was recorded with KBr on a FTIR-8400S Shimadzu. TG analysis was carried out in an air

atmosphere in the temperature range 30-700 °C using Shimadzu TGA-50 instrument. The powder XRD was carried out using Bruker AXS D8 advance X-ray powder diffractometer with a CuKα (λ=1. 54058) target and movable detector. Scanning electron micrographs (SEMs) of RuY and 5Y were carried out using SEM instrument (model-JSM-5610LV), JEOL to analyze the morphology of the samples. BET surface area and pore volume of the zeolite Y based materials were measured by a multipoint BET method using Micromeritics, ASAP 2010 surface area analyzer. Atomic absorption spectra (AAS) of filtrate were recorded on a PerkinElmer 4100-1319. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of both ligands were carried out by Varian- Gemini (200 MHz) instrument using MeOD and CDCl<sub>3</sub> as a solvent, respectively. The magnetic property of neat metal complexes was measured by the magnetic susceptibility balance of models Johnson Matthey & Sherwood.

#### 2.3 Synthesis section

The synthetic pathway of ligands (1, 2), neat metal complexes (3-6), metal exchanged zeolite Y (RuY and Fe), and zeolite Y encapsulated complexes (3Y-6Y) are demonstrated in scheme 1.

#### 2.3.1 Preparation of ligands 1 and 2

2-hydroxybenzaldehyde and/or 2-hydroxy-5-nitrobenzaldehyde of two molar ratios dissolve in methanol in a two-neck round bottom flask and refluxed for 15 min. Subsequently; one molar ratio of diethylenetriamine was added dropwise and refluxed again for 1 h at 70 °C. The movement of the reaction was verified by using TLC with the appropriate solvent system. Once the reaction completed, the excess of methanol was evaporated and an oily reddish product was obtained in the case of ligand 1. In preparation of ligand 2, a red crystalline solid product was filtered and washed with methanol and dried in air. Moreover, the purity of the ligand 1 and 2 was analyzed using IR and UV-Vis spectroscopic techniques. Ligand 1: reddish oily liquid, yield 89.2%, <sup>1</sup>H NMR (200 MHz, MeOD):  $\delta$  (ppm) 8.21 (2H, s, –OH),  $\delta$  3.73 (4H, t, HC=N–CH<sub>2</sub>),  $\delta$  3.28 (4H, q, –H<sub>2</sub>C–NH),  $\delta$  7.89 (2H, s, –HC=N),  $\delta$  2.98 (1H, t, –NH),  $\delta$  7.39- 6.63 (8H, m, aromatic protons); <sup>13</sup>C NMR (200 MHz, MeOD)  $\delta$ (ppm): 49.6 (–CH<sub>2</sub>–NH–), 58.5 (=C=N–CH<sub>2</sub>–), ~117.2, ~120.8, ~121.9, ~132.8, ~133.4 (carbons of the aromatic ring

moiety), 162.2 (–<u>C</u>–OH), 168.6 (–<u>C</u>=N). Ligand 2: red crystalline solid, yield 94.6%, <sup>1</sup>H NMR (200 MHz, MeOD)  $\delta$  (ppm): 3.03 (4H, q, –<u>H</u><sub>2</sub>C–NH), 2.79 (1H, t, –N<u>H</u>), 3.83 (4H, t, HC=N–C<u>H</u><sub>2</sub>), 7.97-6.69 ppm (6H, dd, aromatic protons) 8.56 (2H, s, –<u>H</u>C=N), 8.89 (2H, s, –C–O<u>H</u>); <sup>13</sup>C NMR (200 MHz, MeOD)  $\delta$ : 48.4 (–<u>C</u>H<sub>2</sub>– NH–), 52.5 (=C=N–<u>C</u>H<sub>2</sub>–), ~114.3, ~122.5, ~122.8, ~128.2 139.1 (carbons of the aromatic ring moiety), 153.5(–<u>C</u>–OH), 179.5 (–<u>C</u>=N).

### 2.3.2 Preparation neat Fe(III) and Ru(III) complexes (3-6)

The neat metal complexes were synthesized by the addition of a methanolic metal salt solution (1.25 mmol of RuCl<sub>3</sub>·3H<sub>2</sub>O and/or Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) to the well stirred methanolic solution of the ligand 1 and/or 2 (1.25 mmol). The resulting reaction medium was refluxed with continuous stirring on a water bath for 4 h. The obtained solid products were filtered, washed with methanol, recrystallize with chloroform, and then finally dried in vacuum at 60 °C.

#### 2.3.3 Preparation of metal exchanged RuY and FeY

A mixture of 6 g of the zeolite Y and 1 mmol of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.242 g) and/or Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.403 g) solution in deionized water was stirred under reflux at 110 °C for 16 h. The pH of the reaction medium was adjusted within 4.0–4.5 using buffer tablets in order to avert the formation of respective metal hydroxides. The slurry was then filtered, washed with deionized water to take out the excess of metal ions (inveterate by AAS), chlorides, and/or nitrate ions, and finally dried overnight in an oven at 100–110 °C.

### 2.3.4 Preparation zeolite Y encapsulated metal complexes (3Y-6Y)

Zeolite Y encapsulated complexes were prepared by the 'flexible ligand' method [34]. A stoichiometric excess amount of the ligand 1 and/or 2 was allowed to diffuse through the supercages of the pre-metal exchanged zeolite Y (RuY and FeY) which form a metal complex in its supercages. The mixture was then refluxed for 16 h under constant stirring. The change in the color of solid mass after reaction gives preliminary clue about the formation of complexes inside the supercages of zeolite Y. The slurry was then filtrated, washed frequently with water and dried at room temperature under vacuum. To

remove the unreacted excess ligands and the complexes formed on the surface of the zeolite Y, the resultant products were further purified by Soxhlet extractor using various solvents such as methanol, acetonitrile, chloroform, and DMF until a colorless filtrate was obtained in each case. Finally, the products were dried under vacuum and kept in a muffle furnace overnight at 80–110 °C to obtain anhydrous encapsulated complexes.

#### 2.3.5 Catalytic activity

To carry out the catalytic oxidation of limonene, styrene,  $\alpha$ -Pinene, and cyclohexene, the catalyst (12.5 mg) was initially stirred for 10 min with substrate (25 mmol), subsequently, a solution containing the stoichiometric amount of 30% H<sub>2</sub>O<sub>2</sub> (25 mmol) and 6 ml of acetonitrile was added dropwise to it. The resulting catalytic medium was reacted with continuous stirring on an oil bath at 353 K for 18 h. The zeolite Y based heterogeneous catalysts could be extracted by simple filtration and reused for several times, whereas the neat metal complexes were found to be degraded during the catalytic study. Besides that, the crude reaction mixture (filtrate) was quantitatively analyzed by gas chromatography.

#### 3. Results and discussion

### 3.1 Powder X-ray Diffraction (XRD) Studies

To confirm the conservation of the zeolite Y framework and the encapsulation of metal complexes inside the supercages of zeolite Y, the powder XRD of pure NaY, FeY, RuY, 3Y-6Y, and recycled 5Y (denoted as  $5Y^{R1}$ , used once over  $\alpha$ -pinene oxidation) were recorded. As shown in figure 1, analogous XRD patterns of pure NaY, FeY, RuY, 3Y-6Y, and  $5Y^{R1}$  indeed signpost the preservation of the zeolite Y framework during the ion exchange, encapsulation, and even during the catalytic study. Nonetheless, a marked variance is observed in the XRD of 3Y-6Y and  $5Y^{R1}$  from that of the pure zeolite Y, FeY, and RuY in the relative intensities of peak positions of  $I_{2 \ 2 \ 0}$  and  $I_{3 \ 3 \ 1}$  reflections appearing at 10° and 12°, respectively. In the case of pure NaY, FeY, and RuY, the relationship  $I_{220} > I_{311}$  retained, whereas, in the case of 3Y-6Y and  $5Y^{R1}$ ,  $I_{311} > I_{220}$  is observed. This alteration in the intensities is may be due to the rearrangement of randomly coordinated free cations and the existence of a large metal complex within the supercages of zeolite Y [35-37].

#### 3.2 Scanning electron microscopy

The formation of metal complexes is basically targeted inside the supercages of zeolite Y; however, some uncoordinated ligands and complex can always be there on the peripheral surface of zeolite Y during the synthesis of 3Y-6Y. As shown in the figure 2 some redundant particles such as uncoordinated ligands and the complexes are visible on the surface of zeolite Y in the SEM of 5Y taken before the soxhlet extraction. To minimize the leaching of surface redundant particles during the utilization of these materials as catalysts, each zeolite-Y encapsulated complex was extensively purified by soxhlet extractor using various solvents (methanol, acetonitrile, chloroform, and DMF) until the filtrate becomes colorless and free from any metal ions (confirmed by AAS). In the SEM of finished products 5Y (after soxhlet extraction), no surface complexes or ligands are seen and the particle boundaries on the peripheral surface of zeolite Y is clearly discernible, which indicate an effective removal of redundant particles from the peripheral surface of zeolite Y [34, 38]. Besides, no new crystalline patterns are seen in the SEM of 5Y which may be due to fine dispersal of metal complexes inside the supercages of zeolite Y [39].

### 3.3 ICP-AES, Molar conductivity, and BET surface area analysis

As shown in table 1, elemental analysis data divulges that the Ru(III) and Fe(III) metal ions form a mononuclear neat metal complexes (3-6) with the ligand 1 and/or 2 in equimolar (1:1) ratio by the deprotonation of two phenolic groups present in 1 and/or 2, which is found in an agreement with the theoretical consideration. Furthermore, the lower molar conductivity values (Table 1) suggest non-ionic nature of each neat metal complex that clearly indicates that monodentate uninegative (Cl<sup>-1</sup> in 5 and 6, NO<sup>-3</sup> in 3 and 4) ligand must be present in the coordination sphere of complexes along with chelating ligand 1 and/or 2. In addition, the negative result of qualitative analysis for Cl<sup>-1</sup> (In 5 and 6) and NO<sup>-3</sup> (In 3 and 4) reinforce the non-ionic nature of each neat metal complex [40, 41].

The Si and Al content (%) in each zeolite Y based nanohybrid material is rather different (due to variation in the water content, see TGA); however, the similar Si/Al ratio (Table 2) in each catalyst signpost the absence of dealumination and it also supports

the fact that no destruction has occurred in the zeolite Y framework upon ion exchange, encapsulation and even during the catalytic study. The prepared catalysts 3Y-6Y were treated with the 0.01 M NaCl immediately after the soxhlet extraction in order to replace the extra uncoordinated Fe(III) and/or Ru(III) by Na(I) but the higher M/C ratio in the 3Y-6Y compared (Table 2) to 3-6 (Table 1) indicate that a little extra amount of uncoordinated Fe(III) and/or Ru(III) ions are still remains in the supercages of zeolite Y. The decrease in the quantity of Fe(III) and Ru(III) in the 3Y-5Y compared to FeY and RuY could be recognized to either the coordination of metal ion in the formation of metal complexes inside the supercages of zeolites or metal ion leaching during the encapsulation. The presence of carbon and nitrogen in 3Y-6Y, 5Y<sup>R1</sup>, and 5Y<sup>R11</sup> with almost similar C/N ratio to that of their homogeneous counterparts 3-6 evidently supports the presence of organic moiety inside the supercages of zeolite Y.

The encapsulation of metal complexes inside the supercages of zeolite Y can also be confirmed by BET surface area analysis. As presented in table 2, upon ion exchange of zeolite Y with Ru(III) and/or Fe(III), only a minor reduction in the surface area and pore volume (13-15%) is observed, whereas a drastic fall in the surface area and pore volume (60-50%) in 3Y-6Y undoubtedly specify the formation of bulky metal complexes inside the supercages of zeolite Y.

Interestingly, the absence of nitrogen, inferior concentration of carbon (Table 2) and the minor weight loss up to 700 °C in the TGA of 5Y<sup>R12</sup> (Where 5Y<sup>R12</sup> is catalyst 5Y dehydrated at 600 °C prior to the analysis) supports the fact that chelating ligands has already been removed as a gases (CO<sub>2</sub>, NO, NO<sub>2</sub>) from zeolite Y by complex decomposition during the dehydration, whereas no considerable deviation in the surface area and pore volume was observed upon dehydration (Table 2) This could be accredited to the formation of respective metal oxide from chelate complex inside the supercages zeolite Y at high temperature, which halts the surface area and pore volume to loss of bulky chelating ligands from the supercages of zeolites.

3.4 Infrared spectroscopy

The FTIR spectra of ligands 1 and 2 mainly exhibit characteristic bands in the region 1636-1600 and 3600-3250 cm<sup>-1</sup> (Weak broad band due to H-bonding) due to  $v_{(C=N)}$  and  $v_{(O-H)}$ , respectively. As shown in figure 3,  $v_{(C=N)}$  band is shifted toward lower wavenumbers (1616-1587 cm<sup>-1</sup>) in the neat metal complexes compared to their respective ligands, which demonstrate the coordination of azomethine nitrogen with a transition metal ion. A weak  $v_{(O-H)}$  broadband present at 3600–3250 cm<sup>-1</sup> in ligand 1 and/or 2 might have disappeared in 3-6 due to coordination of phenolic –OH to a metal ion via deprotonation; however, the presence of extra strong broad bands in the region of 3600–3250 cm<sup>-1</sup> clearly signpost the presence of crystal water molecules in each neat complexes, further supported by TG analysis [42]. The coordination of -NH group to metal ion could not be resolute due to the presence of broadband of crystal water in the region of 3600–3250 cm<sup>-1</sup> where –NH group normally exhibits [43]. Furthermore, the appearances of new weak broad band (Due to overlapping of U(M-O)phenolic, U(M-N) azomethine,  $\upsilon_{(M-N) - NH \text{ group}}$  and  $\upsilon_{(M-CI)}$  and/or  $\upsilon_{(M-NO3)}$  bands) in the low frequency region of 600–400 cm<sup>-1</sup> specify the coordination of azomethine nitrogen, phenolic –OH, –NH group, and  $CI^{-1}$  (in 5 and 6) and/or  $NO_3^{-1}$  (in 3 and 4) to the transition metal ion [43-45].

As shown in the figure 3, zeolite Y, RuY, FeY, 3Y-6Y, 5Y<sup>R1</sup>, 5Y<sup>R1</sup>, and 5Y<sup>R12</sup> mainly exhibit bands nearly at 3600-3200, 1640, 1056, 816, 448, 600, 1200, and 672 cm<sup>-1</sup> due to surface –OH group, lattice water molecules,  $v_{asym}T$ –O (internal),  $v_{sym}T$ –O (internal),  $v_{bend}T$ –O (internal), double ring external linkage,  $v_{asym}T$ –O (external), and  $v_{sym}T$ –O (external, T= Si, Al), respectively [46]. In 3Y-6Y, the bands exhibited by trapped complexes are covered up by these strong zeolitic bands; however, the presence of weak bands due to trapped complexes in the region 1570-1300 cm<sup>-1</sup> (where the zeolite matrix does not absorb) clearly indicates that the metal complexes are existing inside the zeolite Y supercages. The trivial shifting of these peak positions compared to the respective neat complexes can be accredited to the influence of zeolite Y matrix on the geometry of the encapsulated complexes [27]. The FTIR spectra of the 5Y<sup>R1</sup> and 5Y<sup>R11</sup> (Recycled 5Y dehydrated at 250 and 350 °C, respectively) are found to be extra strong due to the removal of disquieting intrazeolite water molecules which veneer the weak bands exhibited by trapped complexes. In the case of 5Y<sup>R12</sup> (Recycled 5Y dehydrated at 600 C°), the absence of weak bands in the region 1570-1300 cm<sup>-1</sup>

indicates that the trapped complex might have decomposed completely during the prior dehydration. Moreover, the analogous FTIR pattern of zeolite Y, RuY, FeY, 3Y-6Y, 5Y<sup>R1</sup>, 5Y<sup>R1</sup>, and 5Y<sup>R12</sup> (except, the region 1570-1300 cm<sup>-1</sup> in 3Y-6Y, 5Y<sup>R1</sup> and 5Y<sup>R11</sup>) support the fact that the zeolite Y framework remains intact upon ion exchange, encapsulation, after being used as a catalyst and even upon dehydration at high temperature [47].

#### 3.5 UV-visible spectroscopy and Magnetic susceptibility measurements

The peak values for the electronic transitions detected in ligands 1 and 2, neat metal complexes 3-6 and modified zeolite Y based materials are presented in table 3. The absorption spectrum of ligand 1 displays two lower energy bands at 400 and 315 nm and three higher energy bands at 254, 213, and 206 nm (Figure 4). The bands at higher wavelength are ascribed to  $n \to \pi^*$  and the bands at lower wavelength are due to  $\pi \to \pi^*$  $\pi^*$  transitions. In the ligand 2, five absorption bands are observed at 392, 318, 229, 212, and 205 nm. The former two bands are attributed to  $n \rightarrow \pi^*$  and the remaining are assigned to  $\pi \to \pi^*$  transition. The neat iron (III) complexes (3 and 4) display absorption peaks above and below 250 nm due to  $\pi \to \pi^*$  and  $n \to \pi^*$  (overlapped by strong *LMCT* in complex) originating from the ligands. In addition to these transitions, the band at 321 nm in complex 3 and band at 323 nm in complex 4 is attributable to the ligand to metal charge transfer transition (*LMCT*), a transition from  $p\pi$  orbitals of phenolate oxygen to the  $d\pi^*$  orbitals of the Fe(III). The existence of an weak additional band in the region of 508-497 nm in 3 and 4 are attributed to  ${}^{6}A_{1g} \rightarrow T_{2g}$  (G) transition (d-d) and the observed magnetic moment value in the range of 5.81-5.69 B.M is a characteristic value of Fe(III) ion in an octahedral geometry [48-52]. The neat Ru(III) complexes (5 and 6) of ligands 1 and 2 exhibits bands below 287 nm (Table 3) due to  $\pi \to \pi^*$  and  $n \to \pi^*$ (dominated by strong *LMCT* in the complex) occurring due to ligands system. The presence of strong band nearly at 339 nm in complex 5 and at 316 nm in complex 6 can be ascribed to the ligand to metal charge transfer (LMCT) transition. Moreover, the existence of very weak low energy d-d band  $({}^{2}T_{2g} \rightarrow {}^{4}T_{2g})$  at 647- 602 nm and lower obtained magnetic moment value (Table 1) mutually suggest an octahedral geometry of both the Ru(III) complexes [53, 54].

As displayed in figure 4, pure zeolite Y commonly features two weak absorption peaks at 306 and 345 nm owing to the charge transfer transition (Al  $\leftarrow$  O) of two different Al–O units present zeolite Y framework [55, 56]. The presence of similar bands at 306 nm in FeY, RuY, and in 3Y-6Y confirmed the absence of dealumination during the synthesis (ion exchange and encapsulation) of these materials. However, in 3Y-6Y, a weak host zeolitic band (345 nm) is exclusively covered by the appearance of new strong charge transfer transition exhibited by the trapped metal complexes.

Besides these zeolitic bands, the presence of weak bands at 655 nm in FeY and at 760 nm in RuY can be recognized as a *d-d* transition, which is characteristic of an octahedral configuration around to M(III) ions designed by oxygens and/or physically or chemisorbed water molecules present in the zeolite Y framework. In the case of 3Y-6Y, the absorption bands due to trapped complexes are less intense than those of the respective neat complexes 3-6 due to its lower concentration inside the supercages of zeolite Y. Nevertheless, the 3Y-6Y exhibits absorption bands nearly at the similar wavelength as those observed in the neat complex 3-6, a slight shifting of the bands towards lower or higher wavelengths are observed either under the influence of zeolite Y matrix or the distortion in the geometry of metal complexes itself upon encapsulation.

#### 3.6 TG analysis

Table 4 demonstrates the thermal activities of synthesized neat and encapsulated complexes on the basis of TG analysis. The TG curve of 3 and 4 undergoes decomposition in three stages (Figure 5). The first stage arises in the temperature ranges of 30-110 °C with the mass loss of 8.0% (cal. 7.8%) in 3 and 6.1% (cal. 6.5%) in 4 due to the removal of two moles of lattice water molecules. In the second stage, which is observed in the range of 111-220 °C, a weight loss of about 11.4% (cal. 13.4%) in complex 3 and 11.9% (cal. 11.2%) in 4 can be attributed to the removal of the monodentate ligand from the complexes. In the third stage, 3 and 4 decompose within the temperature range of 221- 450 °C with the weight loss of about 45.6% (cal. 44.3%) and 52.8% (cal.53.4%), respectively, which is ascribed to the removal of chelating ligands via complex decomposition and leaving behind the ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) as residue. In the case of Ru(III) complexes, 5 shows weight loss of about 3.8 (cal. 3.9), 7.4 (cal. 7.7), and 35.8% (cal. 34.1%) due to the stepwise removal of one mole of lattice

water, monodentate ligand Cl<sup>-</sup>, and chelating ligand in first (30-150 °C) second (151-260 °C) and third (261-500°C) decomposition stage, respectively. As shown in figure 5, complex 6 displays weight loss of about 3.2 % (cal. 3.2%) in the first stage (30-120°C), 6.0% (6.4%) in the second stage (121-240 °C) and 46.2% (cal. 45.0%) in the third stage (241-500 °C) due to elimination of one mole of lattice water, monodentate ligand Cl<sup>-</sup>, and chelating ligand, respectively. Beyond 500 °C, complex 5 and 6 leaves residue about 53.8 (cal. 54.3) and 44.6% (45.4%) of ruthenium oxide, respectively.

In case the of zeolite Y based materials, the thermal decomposition mainly occurs in the temperature range of 30 to 400 °C due to the abstraction of physically and chemisorbed water molecules (10.32-0.39) from the zeolite Y framework [57, 58]. As shown in figure 5 (magnified), the encapsulated complexes (except 5Y<sup>12</sup>) exhibit one more thermal decomposition stage of about 1.90- 1.46 % beyond 450 °C. This minor weight loss can be recognized the existence of only trivial amounts of the metal complex inside the supercages of zeolite Y (Table 4), which is in an agreement with the low percent metal content measured by the ICP-AES. Moreover, the weight loss due to trapped complex is prolonged (up to 450 °C) compared to respective homogeneous counterparts 3-6. This observation indicates that the thermal stability of the complexes is considerably enriched upon its encapsulation into zeolite Y supercages. Moreover, no significant weight loss in 5Y<sup>12</sup> beyond 400 °C clearly (Figure 5) indicates the trapped complex has been decomposed during its dehydration at 600 °C prior to the TG analysis. In view of the above, we may conclude that zeolite Y encapsulated complexes.

#### 4. Catalytic activity

The catalytic oxidation of styrene, cyclohexene, limonene, and  $\alpha$ -pinene was performed in a two-necked 25 ml round bottomed flask. In a typical reaction, 12.5 mg catalyst and the substrate (25 mmol) are initially stirred for 10 min. Subsequently, a solution containing the stoichiometric amount of 30% H<sub>2</sub>O<sub>2</sub> (25 mmol) and 6 ml of acetonitrile is added dropwise into it and equilibrated at 353 K in an oil-bath with continuous stirring for 18 h. The products were collected after 18 h and quantitatively analyzed by GC.

#### 4.1 Oxidation of styrene, cyclohexene, limonene, and $\alpha$ -pinene

The catalytic activity and product selectivity of neat and encapsulated complexes along with ligand 1, 2, zeolite Y, RuY, and FeY for styrene, cyclohexene, limonene, and  $\alpha$ -pinene are presented in table 5, 6, 7, and 8, respectively. A blank experiment carried out without any catalyst shows only 1.1, 2.6, 1.2, and 1.0% conversions of styrene, cyclohexene, limonene, and  $\alpha$ -pinene, respectively. The negligible conversion of styrene, cyclohexene, limonene, and  $\alpha$ -pinene (below 5%) in the presence of ligand 1 or 2, and NaY clearly gesture that the zeolite and ligands (1 and/or 2) are futile alone for the catalytic purpose. Despite the fact that the use of RuY and FeY as catalyst displays high TOF about 316-188 h<sup>-1</sup> which is more than 3-fold to that of the homogeneous complexes 3-6, it shows much lower conversions (22-12%) of styrene, cyclohexene, limonene, and  $\alpha$ -pinene to the neat metal complexes 3-6.

As shown in table 5, neat metal complexes 3-6 shows the higher conversion of the styrene as compared to their respective zeolite-Y encapsulated complexes 3Y-6Y; however, it shows lower TOF (52-41 h<sup>-1</sup>) and cannot be recycled as well. In the case of 3Y-6Y, which has shown a much higher TOF in the range of 2130-936 h<sup>-1</sup> and offered high selectivity towards benzaldehyde (93.6-86.8%), a lower conversion (81.2-62.3%) of styrene was observed compared to their homogeneous counterparts 3-6 (100-70.1%). The high selectivity towards benzaldehyde and moderate styrene conversion shown by 3Y-6Y could be attributed to the shape selectivity and high diffusion resistance of styrene through the small windows of zeolite Y, respectively [59]. Styrene oxidation mostly results into benzaldehyde as a major product due to a later nucleophilic attack of H<sub>2</sub>O<sub>2</sub> on pre-formed styrene oxide [60-62]. Other minor products such as 1-phenylethane-1,2-diol and phenylacetaldehyde are formed due to hydrolysis and isomerization of styrene oxide, respectively.

As presented in table 6, the 3-6 achieved high cyclohexene conversions up to 97.5-71.4%, whereas, 3Y-6Y showed lower conversions up to 84.4-64.0% with higher TOF (2351-970 h<sup>-1</sup>) compared to 3-6 (50-41 h<sup>-1</sup>). Even though the use of H<sub>2</sub>O<sub>2</sub> as an oxidant, usually gives cyclohexene oxide as a major product via epoxidation, in the present work, both homo 3-6 and heterogeneous catalysts 3Y-6Y affords higher

selectivity towards Cyone and Cyol around 81-70%, suggesting that the reaction mainly proceeds via the radical pathway.

As observed in the case of cyclohexene and styrene, the heterogeneous catalysts 3Y-6Y are not as efficient (81.6-55.5%) as homogeneous catalysts 3-6 (96.6-69.0%) for limonene oxidation (Table 7); however, it shows high TOF around 2273-1028 h<sup>-1</sup>, which is more than 30-fold to that of 3-6. Moreover, both homo- and heterogeneous catalysts are highly selective towards the formation of allylic products (95-80%) such as carveol and carvone with a minor yield of epoxidation products (20-5%) like limonene oxide, limonene dioxide, and limonene glycol.

In the case of  $\alpha$ -pinene oxidation, table 8, catalyst 3-6 are found to be more active (81.3-54.4%) than the heterogeneous catalyst 3Y-6Y (72.6-56.8%) but the TOF of 3Y-6Y catalysts (2023-816 h<sup>-1</sup>) are grander than the 3-6 catalysts (42.34-31.75 h<sup>-1</sup>). Furthermore, these two types of catalysts are extremely selective towards the allylic products verbenol, verbenone, and myrtenol with the trace amount pinene oxide and campholenal.

Generally, oxidation of cyclohexene, limonene, and  $\alpha$ -pinene can occur on allylic C–H bond or onto C=C bond or can occurs on both sites simultaneously, which can lead a number of products that are difficult to separate out at the end of reaction. As shown in table 6, 7, and 8, the higher selectivity of neat metal complexes 3-6 and zeolite-Y encapsulated complexes 3Y-6Y towards allylic products (Cyol, Cyone, Col, Cone, Vol, Vone, and Mnol) clearly indicate that our catalysts are facilitating allylic oxidation of said the substrates over their epoxidation. The common activity trends for 3-4, RuY, FeY, and 3Y-6Y catalysts derived on the basis of % conversion are found to be different for each substrate and therefore it is difficult to find out the most active catalyst among them. Consequently, the common activity trend derived on the basis of turn over frequency (TOF), which is defined as moles of substrate converted per mole of active metal ion per hour, is found a more suitable trend to pick up the most active catalyst among all. The activity trend of each catalysts on the basis of TOF for styrene, cyclohexene, limonene, and  $\alpha$ -pinene is 4 < 3 < 6 < 5 < FeY < RuY < 4Y < 3Y < 6Y < 5Y. The above activity trend is further supported by the data of H<sub>2</sub>O<sub>2</sub> conversion and H<sub>2</sub>O<sub>2</sub> efficiency whose reaction was carried out separately at identical reaction

condition. As shown in table 5, the H<sub>2</sub>O<sub>2</sub> % conversion is found to be 14.1% at 353 K due to its self-decomposition at reaction temperature (353 K) and it remains almost similar even after the addition of ligand 1, and/or 2, and/or NaY, suggesting ineffectiveness of ligands and zeolite-Y framework in the decomposition of H<sub>2</sub>O<sub>2</sub>. The use of RuY, FeY, 3-6, and 3Y-6Y significantly upsurges the conversion of H<sub>2</sub>O<sub>2</sub> that demonstrate its imperative role in catalyzing the substrate; however, higher H<sub>2</sub>O<sub>2</sub> efficiency of 3-6 and 3Y-6Y could be attributed to the formation of an active chelate intermediate which can easily attack less hinder site of the substrate (allylic C–H) and leads high conversion and the selectivity.

Moreover, the presence of electron withdrawing groups (Nitro) at the para position to the hydroxyl group in complexes of ligand 2 (4, 6, 4Y and 6Y) drops an electron density at ligating "Oxygen" atom in complexes that give rise to an electron deficient metal center compared to the complex of ligand 1 having no electron withdrawing group (R=H) [63, 64]. Subsequently, 3, 5, 3Y, 5Y can be easily oxidized compared to the 4, 6, 4Y and 6Y and therefore found highly active (higher TOF) and selective. Amongst all, encapsulated complex 5Y is found to be a most active catalyst and therefore it was taken as a representative catalyst to check the stability, recyclability, and the effect of H<sub>2</sub>SO<sub>4</sub> on oxidation of styrene, cyclohexene, limonene, and  $\alpha$ -pinene at identical reaction condition.

#### 4.2 Stability and recyclability of the catalyst

The stability and reusability of 5Y were inspected on  $\alpha$ -pinene oxidation at identical reaction condition. The catalyst 5Y was revived by filtration, purified by soxhlet extractor using acetonitrile, and then dried at different temperatures such as 250, 350, and 600 °C (denoted as 5Y<sup>R1</sup>, 5Y<sup>R11</sup> and 5YR<sup>12</sup>, respectively, Table 8) to notice the effect of catalyst dehydration upon its activity and selectivity. In the case of 5Y<sup>R1</sup> and 5Y<sup>R11</sup>, the  $\alpha$ -pinene conversion slightly upsurges (Table 8) due to the removal of an intrazeolite water molecule from the small windows of zeolite Y which reduce the diffusion resistant for the reacting substrate during the catalytic reaction. A drastic fall in the  $\alpha$ -pinene conversion using 5YR<sup>12</sup> clearly indicates that the active trapped complex has decomposed during its dehydration at 600 °C prior to catalytic activity, further supported by FTIR (Figure 3), TGA (Figure 5), and ICP-OES analysis (Table 2). Consequently, the

encapsulated complexes are found to be highly active, selective, and stable at current reaction condition. Moreover, two consecutive runs of 5Y (Table 8, denoted as  $5Y^{R3}$  and  $5Y^{R4}$ , dehydrated at 250 °C prior to the reaction) show no significant loss in the  $\alpha$ -pinene conversion and selectivity of the products. Moreover, the AAS did not show any ruthenium metal content in the filtrate and approves no leaching of metal ions from the catalyst during  $\alpha$ -pinene oxidation.

4.3 Impact of  $H_2SO_4$  on styrene, cyclohexene, limonene, and  $\alpha$ -pinene oxidation An impact of  $H_2SO_4$  on styrene, cyclohexene, limonene, and  $\alpha$ -pinene oxidation catalyzed by 5Y was studied at identical reaction condition. As shown in figure 6, the addition of 2.5 mmol of sulfuric acid during the styrene oxidation boost up the rate of reaction and yield 100% styrene conversion in only 8 h with Bzald (28.0), Styo (57.5), Phetdiol (13.1), and Phacetal (1.4%). On continuing reaction up to 18 h, the selectivity of styrene oxide drops to 9.2%, whereas, the selectivity of Phetdiol (19.1), Phacetal (3.2%) and Bzald (68.5) upsurge due to hydrolysis, isomerization and later nucleophilic attack of  $H_2O_2$  on Styo, respectively [60-62].

In the case of cyclohexene (Figure 7), limonene (Figure 8) and  $\alpha$ -pinene (Figure 9) oxidation, the addition 2.5 mmol of H<sub>2</sub>SO<sub>4</sub> catalyzed by 5Y yield 100% conversions only in 12-10 h that may take more than 18 h to complete the reaction without sulfuric acid. Interestingly, the addition of H<sub>2</sub>SO<sub>4</sub> mainly produces epoxidation products, whereas allylic products are obtained as major products in the absence of H<sub>2</sub>SO<sub>4</sub>. Moreover, on continuing reaction up to 18 h after 100% conversion of cyclohexene limonene and  $\alpha$ -pinene with H<sub>2</sub>SO<sub>4</sub>, the selectivity of allylic alcohols (CyOl, Vol, and Col) and the epoxides (Cyox, Limox, and Piox) decreases gradually due to its farther oxidation into the respective allylic ketones (Cyone, Vone, and Cone) and diols or aldehydes (Cydiol, Limgly, and Camal), respectively.

The catalyst 5Y was recovered by filtration, washed with acetonitrile, dried at 250 °C and then used as a catalyst in the subsequent catalytic run to notice whether the use of 2.5 mmol H<sub>2</sub>SO<sub>4</sub> during the first catalytic cycle has affected on activity of the catalyst or not. As presented in table 9, the successive runs of catalyst 5Y lead to a considerable lowering in the conversion of  $\alpha$ -pinene. This lowering in the catalytic activity can be attributed to a minor distraction of the zeolite-Y encapsulated complexes

under the influence of strong oxidizer caro"s acid which is produced *in situ* by the reaction of H<sub>2</sub>SO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> during the catalytic oxidation. Moreover, we could not recover the catalyst 5Y when 25 mmol H<sub>2</sub>SO<sub>4</sub> was used instead of 2.5 mmol H<sub>2</sub>SO<sub>4</sub>.

From the above observation, it can be concluded that the use of catalytic amount of H<sub>2</sub>SO<sub>4</sub> (2.5 mmol) may help to increase the rate of the oxidation reaction and selectivity of epoxidation products but it decreases the stability and activity of the catalyst in their successive catalytic runs. This lowering in the activity of the catalyst 5Y could only be attributed to the degradation of zeolite-Y encapsulated complexes in the highly acidic reaction medium. Moreover, the possibility of H<sub>2</sub>SO<sub>4</sub> to react with hydroxyl (-OH) and amine (-NH<sub>2</sub>) of ligands can be excluded as the used complex has no free hydroxyl group and an amine group to react with acid or any substrate that is being used throughout the catalytic oxidation.

#### 5. Plausible reaction pathway of catalysts

The reaction mechanism for oxidation catalyzed by Fe(III) complexes with H<sub>2</sub>O<sub>2</sub> has been studied over the last two decades and the involvement of metal hydroperoxide Fe(IV)–OOH has been anticipated as an active intermediate [65, 66]. At the same time, the involvement of metal-oxo species such as M(IV)=O and/or M(V)=O, which are usually resulted by homo- or heterolytic –O–O– bond cleavage of sluggish oxidant Fe(IV)–OOH, has also been anticipated as an active intermediate [67-71]. Moreover, Fujii et al. inveterate Fe(III)-monophenoxyl radical as potent oxidizing species for Fe salen complex at very low temperature (193 K); however, the possibility of Fe(III)monophenoxyl radical can be ruled out here in our case as our reaction temperature is very close to 353 K [72, 73].

In order to figure out the possible reaction pathway,  $10^{-3}$  M solutions of 3- 6 are first dissolved in the least possible amount of methanol and treated distinctly with a methanolic solution of H<sub>2</sub>O<sub>2</sub>. The change in the spectra of 3- 6 by the addition of methanolic H<sub>2</sub>O<sub>2</sub> is studied by UV–Vis spectroscopy (Figure 10). The constant addition of H<sub>2</sub>O<sub>2</sub> to the solution of 3-6 parades a decrease in intensity of the peaks at 497 and 321 nm in 3, 508 and 323 nm in 4, 603 and 339 nm in 5, 647 and 316 nm in 6, whereas an elevation in the intensity of peaks below 300 nm in 3-6 complexes are observed. The

appearance of an isobestic point at 308 nm in 3, at 296 nm in 4, at 295 nm in 5, and at 311 nm in 6, decrease in intensity of the *MLCT* and *d*–*d* bands upon addition of H<sub>2</sub>O<sub>2</sub> can be attributed the direct interaction of H<sub>2</sub>O<sub>2</sub> with M(III) and its transformation into M(IV/V) oxo intermediates. In the case of 3Y-6Y, the detail mechanistic study cannot be carried out due to the lower concentration of complexes inside the supercages of zeolite Y; however the involvement of M(IV)=O or M(V)=O may be predicted due to restraint in dimerization of complexes executed by zeolite-Y nanopores.

In our case, predominant allylic oxidation of cyclohexene (Table 6), limonene (Table 7), and  $\alpha$ -pinene (Table 8) clearly indicate that the reaction is radical type reaction (without H<sub>2</sub>SO<sub>4</sub>), which is instigated by homolytic –O–O–bond cleavage of metal hydroperoxide. Interestingly, the predominant epoxidation instead of allylic oxidation with H<sub>2</sub>SO<sub>4</sub> may infer that the reaction is not a radical type and may proceed via electrophilic M(V)=O intermediate formed by H<sup>+</sup> promoted heterolytic –O–O– bond cleavage of metal hydroperoxide, which further attack on nucleophilic C=C of the substrate and results epoxide as a major product.

As shown in the scheme 2, the reaction of  $H_2O_2$  with complex forms sluggish oxidative metal-hydroperoxide species II. Consequently, the intermediate II undergoes homolytic -O-O bond cleavage and form reactive free radical intermediate III. This highly reactive free radical III immediately attack weak allylic C–H bond of  $\alpha$ -pinene and form intermediate V and VI, which further results into verbenol and myrtenol. The oxidation of verbenol with the help of free radical intermediate III leads to the formation of verbenone as a major product via formation of intermediate IV. In the presence of  $H_2SO_4$ , the proton stimulates the heterolytic -O-O- bond cleavage of intermediate II and form electrophilic intermediate VII, which attack on electron rich site of  $\alpha$ -pinene and form pinene oxide. Moreover, this pinene oxide is converted into campholenal under acidic reaction medium.

#### Conclusion

A novel zeolite Y encapsulated Fe(III) and Ru(III) complexes has been effectively encapsulated by FL method. The encapsulation of metal complexes without any kind of devastation in the zeolite Y framework was assured by FTIR, UV-vis, ICP-AES, powder XRD, TGA, SEMs, as well as BET surface area analysis. In addition to that, respective

neat Fe(III) and Ru(III) homogeneous complexes 3-6 were also synthesized for the sake of comparison with their heterogeneous counterpart 3Y-6Y. It can be concluded that the synthesized catalysts utilized over oxidation of styrene, cyclohexene, limonene, and  $\alpha$ -pinene follows a common activity trend (4 < 3 < 6 < 5 < FeY < RuY < 4Y < 3Y < 6Y < 5Y) which is derived on the basis of TOF and not on % conversions. The identical oxidation reactions carried out for 8, 10, 12, and 12 hrs with H<sub>2</sub>SO<sub>4</sub> using 5Y as representative catalyst yield 100% conversion of styrene, cyclohexene, limonene and  $\alpha$ -pinene with styrene oxide (67.8), cyclohexene oxide (57.3), limonene oxide (55.2) and pinene oxide (57%) as major products with high TOF values, respectively. The encapsulated heterogeneous catalyst could be easily retrieved and used without remarkable loss in the catalytic activity, which makes it grander to neat metal complexes. Furthermore, no metal ion content in the filtrate clearly indicates that no leaching of the metal ion from the catalyst throughout oxidation.

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#### References

- [1] B.A. Arndtsen, R.G Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154.
- [2] J.A. Labinger, J.E Bercaw, Nature 417 (2002) 507.
- [3] K.A. Jorgenson, Chem. Rev. 89 (1989) 431.
- [4] R.A. Sheldon, B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organo-metallic Compounds, VCH, Weinheim, Germany, 2<sup>nd</sup> edn, 2002, pp. 412.
- [5] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, J. Catal. 289 (2012) 259.
- [6] D. Saha, T. Maity, T. Dey, S. Koner, Polyhedron 35 (2012) 55.

- [7] M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, J. Mol. Catal. A: Chem. 258 (2006) 327.
- [8] P. Chutia, S. Kato, T. Kojima, S. Satokawa, Polyhedron 28 (2009) 370.
- [9] B. Meunier, Biomimetic Oxidations Catalyzed by Transition Metal Complexes; Imperial College Press: London, 2000.
- [10] M.A. Bigi, S.A. Reed, M.C White, Nature Chem. 3 (2011) 216.
- [11] A.L. Cánepa, C.M. Chanquía, V.M. Vaschetti, G.A. Eimer, S.G. Casuscelli, J. Mol. Catal. A: Chem. 404–405 (2015) 65.
- [12] F. Ashouri, M. Zare, M. Bagherzade, Inorg. Chem. Commun. 61 (2015) 73.
- [13] A. Najafian, M. Rabbani, R. Rahimi, M. Deilamkamar, A. Maleki, Solid State Sci. 46 (2015) 7.
- [14] S. Rayati, E. Bohloulbandi, C.R. Chimie 17 (2014) 62.
- [15] M. Bagherzadeh, F. Ashouri, M. Đakovic, Polyhedron 69 (2014) 167.
- [16] S. Sha, H. Yang, J. Li, C. Zhuang, S. Gao, S. Liu, Catal. Commun. 43 (2014) 146.
- [17] R. Ji, K. Yub, L.L. Loua, S. Liua, J. Mol. Catal. A: Chem. 378 (2013) 7.
- [18] D. Habibi, A.R. Faraji, Appl. Surf. Sci. 276 (2013) 487.
- [19] S.J.J. Titinchi, H.S. Abbo, Catal. Today 204 (2013) 114.
- [20] S.M. Islam, A.S. Roy, P. Mondal, S. Paul, N.Salam, Inorg. Chem. Commun. 24 (2012) 170.
- [21] B. Monteiro, S. Gago, S.S. Balula, A.A. Valente, I.S. Goncalves, M. Pillinger, J. Mol. Catal. A: Chem. 312 (2009) 23.
- [22] G.R. Reddy, S. Balasubramaniana, K. Chennakesavulu, J. Mater. Chem. A 2 (2014) 15598.
- [23] M. Salavati-Niasari, A. Sobhani, J. Mol. Catal. A: Chem. 285 (2008) 58.
- [24] C.K. Modi, P.M. Trivedi, J.A. Chudasama, H.D. Nakum, D.K. Parmar, S.K. Gupta, P.K. Jha, Green Chem. Lett. Rev. 7 (2014) 278.
- [25] K.K. Bania, R.C. Deka, J. Phys. Chem. C 117 (2013) 11663.
- [26] I.C. Neves, I. Kuz´niarska-Biernacka, A.M. Fonseca, Inorg. Chim. Acta 394 (2013) 591.
- [27] K.B. Kusum, C.D. Ramesh, J. Phys. Chem. C 116 (2012) 14295.
- [28] K.K. Bania, R.C. Deka, J. Phys. Chem. C 115 (2011) 9601.

- [29] M. Salavati-Niasari, Inorg. Chem. Commun. 13 (2) (2010) 266.
- [30] D.R. Godhani, H.D. Nakum, D.K. Parmar, J.P. Mehta, N.C. Desai, J. Mol. Catal. A: Chem. 415 (2016) 37.
- [31] K.K. Bania, G.V. Karunakar, K.Goutham, R.C. Deka, Inorg. Chem. 52 (2013 8017.
- [32] M.R. Maurya, A. Kumar, J.C. Pessoa, Coord. Chem. Rev. 255 (2011) 2315.
- [33] R. Raja, P. Ratnasamy, Appl. Catal. A. 143 (1996) 145.
- [34] K.K. Bania, D. Bharali, B. Viswanathan, R.C. Deka, Inorg. Chem. 51 (3) (2012) 1657.
- [35] M. Jafarian, M. Rashvandavei, M. Khakali, F. Gobal, S. Rayati, M.G. Mahjani, J. Phys. Chem. C, 116 (2012) 18518.
- [36] W.H. Quayle, J.H. Lunsford, Inorg. Chem. 21 (1982) 97.
- [37] W.H. Quayle, G. Peeters, G.L. De Roy, E.F. Vansant, J. H. Lunsford, Inorg. Chem.21 (1982) 2226.
- [38] I. Kuz´niarska-Biernacka, M.A. Carvalho, S. B. Rasmussen, M. A. Bañares,
   K.Biernacki, A.L. Magalhães, A.G. Rolo, A.M. Fonseca, I.C. Neves, Eur. J. Inorg.
   Chem. 2013, 5408–5417
- [39] S.P. Varkey, C. Ratnasamy, P. Ratnasamy, J. Mol. Catal. A: Chem. 135 (1998) 295.
- [40] T.A. Yousef, G.M. Abu El-Reash, O.A. El-Gammal, R.A. Bedier, J. Mol. Str. 1035 (2013) 307.
- [41] E. Wiberg, A.F. Holleman, Inorganic Chemistry, Elsevier, 2001 ISBN 0-12-352651-5.
- [42] M.S. Refat, J. Mol. Str. 842 (2007) 24.
- [43] M.R. Maurya, S.J.J. Titinchi, S. Chand, J. Mol. Catal. A: Chem. 193 (2003) 165.
- [44] L.F. Vilas Boas, J. Costa Pessoa, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 3, Pergamon Press, Oxford, 1987, pp. 453.
- [45] A. Hatzidumitrious, C.A. Bolos, Polyhedron, 17 (1998) 1779.
- [46] C. Jin, W.B. Fan, Y.J Jia, B.B Fan, J. H Ma, R. F. Li, J. Mol. Catal. A: Chem. 249 (2006) 23.
- [47] H.S. Abbo, S.J.J. Titinchi, Top. Catal. 53 (2010) 254.

- [48] M.R. Maurya, S.J.J. Titinchi, S. Chand, I.M. Mishra, J. Mol. Catal. A: Chem. 180 (2002) 201.
- [49] B.P. Gaber, V. Miskowski, T.G. Spiro, J. Am. Chem. Soc. 96 (22) (1974) 6868.
- [50] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, "Advanced Inorganic Chemistry", 6th ed., Wiley, New York, 1999.
- [51] R.D. Patton' L.T. Taylor, Inorg. Chim. Acta, 8 (1974) 191.
- [52] G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 1, Pergamon Press, Oxford, 1987, p. 253.
- [53] M.M.T. Khan, S.A. Mizra, Z.A. Shaikh, Ch. Sreelatha, P. Paul, R.S. Shukla, D. Srinivas, A.P. Rao, S.H.R. Abdi, S.D. Bhatt, G. Ramachandraiah, Polyhedron 1 (1992) 1821.
- [54] B.H. Mehta, J.A. sheikh. J Ind Council Chem. 26 (2009) 1.
- [55] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Company, Amsterdam, 1968
- [56] E.D. Garbowski, C.J. Irodatas, Phys. Chem. 86 (1982) 97.
- [57] G. Meyer, D. Woehrle, M. Mohl, G. Schulz-Ekloff, Zeolites 4 (1984) 30.
- [58] H. Diegruber, P.J. Plath, G. Schulz-Ekloff, M. Mohl, J. Mol. Catal. 24 (1984) 115.
- [59] S.M. Csicsery, Zeolites 4 (1984) 202.
- [60] I. Kuzniarska-Biernacka, A.M. Fonseca, I.C. Neves, Inorg. Chim. Acta 394 (1) (2013) 591.
- [61] J.D. Bass, A. Solovyov, A.J. Pascall, A. Katz, J. Am. Chem. Soc. 128 (2006) 3737.
- [62] V. Hulea, E. Dumitriu, Appl. Catal. A: Gen. 277 (2004) 99.
- [63] Y. Sulfab, F.M. Al-Sogair, Trans. Met. Chem. 27 (2002) 299.
- [64] T. Krebs, E. Glaser, T. Bill, W. Meyer-Klaucke, K. Wieghradt, Angew. Chem. Int. Ed. 38 (1999) 359.
- [65] A. Wada, S. Ogo, S. Nagatomo, T. Kitagawa, Y. Watanabe, K. Jitsukawa, H. Masuda, Inorg. Chem. 41 (2002) 616.
- [66] Y.M. Kim, K.B. Cho, J. Cho, B. Wang, C. Li, S. Shaik, W. Nam, J. Am. Chem. Soc. 135 (2013) 8838.
- [67] W. Nam, Acc. Chem. Res. 40 (2007) 522.
- [68] M.J. Park, J. Lee, Y. Suh, J. Kim, W. Nam, J. Am. Chem. Soc. 128 (2006) 2630.

- [69] A. Franke, C. Fertinger, R. van Eldik, Chem. Eur. J. 18 (2012) 6935.
- [70] V. K. Sivasubramanian, M. Ganesan, S. Rajagopal, R. Ramaraj, J. Org. Chem. 67(5) (2002) 1506.
- [71] A.M.I. Jayaseeli, S. Rajagopal, J. Mol. Catal. A: Chem. 309 (2009) 103.
- [72] T. Kurahashi, Y. Kobayashi, S. Nagamoto, T. Tosha, T. Kitagawa, H. Fujji, Inorg. Chem. 44 (22) (2005) 8156.
- [73] T. Kurahashi, K. Oda, M. Sigimoto, T. Ogura, H. Fujji, Inorg. Chem. 45 (2006) 7709.

#### Figure and scheme Captions

**Figure 1.** Powder X-ray Diffraction (XRD) patterns pure NaY, FeY, RuY and zeolite Y encapsulated complexes (3Y- 6Y).

**Figure 2.** Scanning electron micrographs of RuY and 5Y before soxhlet and after soxhlet extraction.

**Figure 3.** FTIR spectra of ligands (1 and 2), neat complexes (3-6), FeY, RuY, and zeolite Y encapsulated complexes (3Y- 6Y).

**Figure 4.** Electronic spectra of ligands (1 and 2), neat complexes (3-6), FeY, RuY, and zeolite Y encapsulated complexes (3Y- 6Y).

**Figure 5.** TGA patterns of neat complexes (3-6), FeY, RuY, and zeolite Y encapsulated complexes (3Y- 6Y).

**Figure 6.** Influence of reaction time on styrene conversion and product selectivity with their respective TOF values. Reaction condition: 25 mmol styrene, 25 mmol 30%  $H_2O_2$ , 12.5 mg catalyst 5Y, 2.5 mmol (0.13 ml) of  $H_2SO_4$ , 6 ml of acetonitrile, 353 K.

**Figure 7.** Influence of reaction time on cyclohexene conversion and product selectivity with their TOF values. Reaction condition: 25 mmol cyclohexene, 25 mmol 30%  $H_2O_2$ , 12.5 mg catalyst 5Y, 2.5 mmol (0.13 ml) of  $H_2SO_4$ , 6 ml of acetonitrile, 353 K.

**Figure 8.** Influence of reaction time on limonene conversion and product selectivity with their TOF values. Reaction condition: 25 mmol limonene, 25 mmol 30%  $H_2O_2$ , 12.5 mg catalyst 5Y, 2.5 mmol (0.13 ml) of  $H_2SO_4$ , 6 ml of acetonitrile, 353 K.

**Figure 9.** Influence of reaction time on  $\alpha$ -pinene conversion and product selectivity with their TOF values. Reaction condition: 25 mmol  $\alpha$ -pinene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg catalyst 5Y, 2.5 mmol (0.13 ml) of H<sub>2</sub>SO<sub>4</sub>, 6 ml of acetonitrile, 353 K.

**Figure 10.** UV–visible spectral studies of neat complexes (3-6) taken during the consecutive addition of a methanolic  $H_2O_2$  (isobestic point were observed, light green arrows).

**Scheme 1.** Synthetic route of the ligands (1 and 2), neat complexes (3-6), FeY, RuY, and zeolite Y encapsulated complexes (3Y- 6Y).

**Scheme 2.** The merely tentative reaction mechanism for oxidation of  $\alpha$ -pinene with H<sub>2</sub>O<sub>2</sub> catalyzed by transition metal complexes.



Figure 1.



Figure 2



Wavenumber (cm<sup>-1</sup>)

Figure 3.



Figure 4.



















Figure 9.



Figure 10.



Scheme 1.



Where M= Ru (III) and/Fe(III), Ligand: 1 and/or 2, X: Cl- or NO<sub>3</sub>-

### Scheme 2.

**Table 1**. Chemical composition and physical properties of ligands (1 and 2), and their respective neat metal complexes (3-6).

Catalyst	Elemental analysis Perce			Percent	tage (%)	Yield	M.P <sup>b</sup>	Λm <sup>c</sup>	µeff		
	%Found	d (calcula	ted)			ratio		(%)	(°C)		(B.M)
	С	Н	Ν	M <sup>a</sup>	0	C/N	M/C	_			
1	68.32	6.96	13.27		11.45	5.14		89.2	-	-	-
	(69.43)	(6.80)	(13.49)	-	(10.28)	(5.14)	-				
2	53.76	4.85	17.40		23.99	3.08		94.6	219	-	-
	(53.86)	(4.77)	(17.45)	-	(23.92)	(3.08)	-				
3	48.00	4.81	12.41	12.45	22.33	3.86	0.25	98.2	>300	07.3	5.81
	(48.56)	(4.75)	(12.58)	(12.54)	(21.56)	(3. 86)	(0.25)				
4	40.87	3.40	15.72	10.61	29.40	2.59	0.25	71.5	>300	12.0	5.69
	(40.39)	(3.48)	(15.70)	(10.43)	(29.89)	(2.57)	(0.25)				
5	46.10	4.51	8.99	21.56	11.04	5.12	0.46	71.3	>300	15.3	1.86
	(46.60)	(4.56)	(9.06)	(21.79)	(10.35)	(5.14)	(0.46)				
6	39.90	3.54	12.81	18.89	18.86	3.11	0.47	65.4	>300	11.4	1.74
	(39.03)	(3.46)	(12.64)	(18.25)	(20.20)	(3.08)	(0.46)				

<sup>a</sup> Respective transition metal Fe(III) or Ru(III).

<sup>b</sup> Melting points (°C),

<sup>c</sup> Molar Conductivity (S cm<sup>2</sup> mol<sup>-1</sup>) of neat metal complex were measured in methanol at 30 °C.

**Table 2**. ICP-AES and BET surface area analysis of pure NaY, FeY, RuY, encapsulated complexes (3Y-6Y), and recycled 5Y catalyst with their possible unit cell formulae.

Catalyst	Unit cell formulae	ICP-AES Elemental analysis (%) Percentage			ntage Ratio	)	Surface	Pore	Loss in				
											area	volume	pore
		С	Ν	Na	M <sup>a</sup>	Si	AI	Si/Al	C/N	M/C	(m²/g)	(cm <sup>3</sup> /g)	volume (%)
NaY	Na <sub>30</sub> [(AIO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]	-	-	5.07	-	33.46	5.95	5.62	-	-	539.0	0.327	-
FeY	Na <sub>26.1</sub> Fe <sub>1.3</sub> [(AIO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]	-	-	4.58	0.555	34.79	6.19	5.62	-	-	472.0	0.282	13.7
RuY	Na27.3Ru0.9[(AlO2)30(SiO2)162]	-	-	4.75	0.688	34.43	6.12	5.62	-	-	463.7	0.276	15.6
3Y	$Na_{27.4}[Fe_{0.86}(1)_{0.61}(AIO_2)_{30}(SiO_2)_{162}]$	1.000	0.260	4.79	0.365	34.65	6.16	5.62	3.84	0.36	206.9	0.139	57.5
4Y	Na27.12[Fe0.96(2)0.59(AIO2)30(SiO2)162]	0.920	0.345	4.75	0.409	34.72	6.17	5.62	2.66	0.44	186.8	0.131	59.9
5Y	$Na_{28.41}[Ru_{0.53}(1)_{0.46}(AIO_2)_{30}(SiO_2)_{162}]$	0.740	0.142	4.92	0.403	34.30	6.10	5.62	5.21	0.54	234.5	0.158	51.7
6Y	$Na_{28.62}[Ru_{0.46}(2)_{0.41}(AIO_2)_{30}(SiO_2)_{162}]$	0.672	0.218	4.99	0.353	34.57	6.15	5.62	3.08	0.52	198.0	0.137	58.1
5Y <sup>R1</sup>	$Na_{28.41}[Ru_{0.53}(1)_{0.46}(AIO_2)_{30}(SiO_2)_{162}]$	0.772	0.149	5.09	0.417	35.46	6.30	5.62	5.18	0.54	239.5	0.163	50.1
5Y <sup>R11</sup>	$Na_{28.41}[Ru_{0.53}(1)_{0.46}(AIO_2)_{30}(SiO_2)_{162}]$	0.797	0.153	5.04	0.424	36.50	6.49	5.62	5.20	0.53	234.5	0.169	48.3
5Y <sup>R12</sup>	Na <sub>28.41</sub> [Ru <sub>0.53</sub> (AlO <sub>2</sub> ) <sub>30</sub> (SiO <sub>2</sub> ) <sub>162</sub> ]	0.010	-	5.29	0.430	36.91	6.56	5.62	-	43.0	265.0	0.184	47.7

<sup>a</sup> Respective transition metal Fe(III) or Ru(III).

5Y<sup>R1</sup>: One time used catalyst 5Y which is dehydrated at 250 °C before ICP-AES and BET analysis.

5Y<sup>R11</sup>: One time used catalyst 5Y which is dehydrated at 350 °C before ICP-AES and BET analysis.

5Y<sup>R12</sup>: One time used catalyst 5Y which is dehydrated at 600 °C before ICP-AES and BET analysis.

Catalyst	Electronic transition	(nm)		
	$\Pi \to \Pi^{\star}$	$n \rightarrow \pi^{\star}$	LMCT	d-d transition
1	206, 213, 254	315, 400	-	-
2	205, 212, 229	318, 392	-	-
3	203, 211, 221, 251	-	321	497
4	210, 218, 224,	291	323	508
5	204, 222, 252	-	339	602
6	201, 208, 224	287	316	647
NaY	-	-	306, 343	-
FeY	-	-	304, 346	655
RuY	-	-	305, 347	760
3Y	209, 219, 238	277	343, 306, 320	450
4Y	214, 221, 229, 246	-	349, 304, 323	481
5Y	208, 225, 235, 241	-	327, 305, 300	581
6Y	206, 222, 245, 256	-	306, 345, 329,	565

**Table 3.** Electronic spectral data of ligands (1 and 2), neat complexes (3-6), NaY, FeY, RuY, and encapsulated complexes (3Y-6Y).

**Table 4.** TGA data of ligands (1 and 2), neat complexes (3-6), and zeolite-Y basedmaterials.

Catalyst	TG range (°C)	Mass loss % obs. (calc.)	Assignment
3	30-110	8.0 (7.8)	<ul> <li>Loss of two crystallization H<sub>2</sub>O</li> </ul>
	111-220	11.4 (13.4)	- Loss of nitrate ligand
	221-500	45.6 (44. 3)	- Removal of Schiff base ligand
	501-700	35.0 (34.5)	- Ferric oxide as residue
4	30-110	6.1 (6.5)	- Loss of two crystallization H <sub>2</sub> O
	111-220	11.9 (11.2)	- Loss of nitrate ligand

	221-450	52.8 (53.4)	- Removal of Schiff base ligand
	451-700	29.2 (28.9)	- Ferric oxide as residue
5	30-150	3.8 (3.9)	- Loss of one crystallization H <sub>2</sub> O
	151-260	7.4 (7.7)	-Loss of chloride ligand
	261-500	35.0 (34.1)	- Removal of Schiff base ligand
	501-700	53.8 (54.3)	- Ruthenium oxide as residue
6	30-120	3.2 (3.2)	- Loss of one crystallization H <sub>2</sub> O
	121-240	6.0 (6.4)	- Loss of chloride ligand
	241-500	46.2 (45.0)	- Removal of Schiff base ligand
	501-700	44.6 (45.4)	- Ruthenium oxide as residue
NaY	30-400	10.32	- Loss of physically and chemisorbed water
FeY	30-400	06.88	- Loss of physically and chemisorbed water
RuY	30-400	7.49	- Loss of physically and chemisorbed water
3Y	30-400	05.35	- Loss of physically and chemisorbed water
	401-700	1.90	- Due to removal of Schiff base
4Y	30-400	4.62	- Loss of physically and chemisorbed water
	401-700	1.46	- Due to removal of Schiff base
5Y	30-400	6.38	- Loss of physically and chemisorbed water
	401-700	1.62	- Due to removal of Schiff base
6Y	30-400	5.85	- Loss of physically and chemisorbed water
	401-700	1.86	- Due to removal of Schiff base
5Y <sup>R1</sup>	30-400	3.52	- Loss of physically and chemisorbed water
	401-700	1.61	- Due to removal of Schiff base
5Y <sup>R11</sup>	30-400	2.43	- Loss of physically and chemisorbed water
	401-700	1.62	- Due to removal of Schiff base
5Y <sup>R12</sup>	30-400	0.39	-Loss of physically and chemisorbed water
	401-700	0.22	- Minor weight loss

5Y<sup>R1</sup>: One time used catalyst 5Y which is dehydrated at 250 °C before TG analysis. 5Y<sup>R11</sup>: One time used catalyst 5Y which is dehydrated at 350 °C before TG analysis. 5Y<sup>R12</sup>: One time used catalyst 5Y which is dehydrated at 600 °C before TG analysis.

Catalyst	Styrene	$H_2O_2$		Product	selectivity	y <sup>f</sup> (%)		Metal <sup>g</sup>	TOF <sup>h</sup>
	conversion (%)	Conv. <sup>d</sup> (%)	effi. <sup>e</sup> (%)	Bzald	Styo	Phetdiol	Phacetal	- (µmoi)	(h <sup>-</sup> ')
blank	1.10	14.1	14.8	68.3	24.2	6.5	1.0	-	-
1	2.91	17.3	16.8	61.2	36.9	1.9	-	-	-
2	2.56	18.5	13.8	67.3	27.1	5.1	0.5	-	-
3	86.2	98.3	87.7	60.5	37.4	0.9	1.2	27.866	43.00
4	70.1	100	57.9	68.9	24.4	4.6	2.1	23.750	41.00
5	100	100	100	67.4	31.2	1.4	-	26.660	52.10
6	77.2	88.2	87.5	63.6	32.2	4.2	-	23.362	45.90
NaY	4.11	16.4	25.0	84.2	09.5	3.1	3.2	-	-
FeY	21.7	76.0	28.5	81.3	12.3	4.2	2.2	1.2420	242.0
RuY	18.7	83.0	22.5	77.8	11.3	8.5	2.4	0.8508	305.0
3Y	81.3	96.0	91.5	86.8	07.1	4.8	1.3	0.8170	1381
4Y	65.7	100	85.7	89.4	05.9	3.2	1.5	0.9155	0936
5Y	76.1	100	76.1	93.6	04.1	2.3	-	0.4984	2130
6Y	62.6	97.2	64.4	90.2	06.1	2.8	0.9	0.4365	1991

Table 5. Oxidation of styrene with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by 1-6, NaY, RuY, FeY, and 3Y-6Y at optimized reaction condition.

<sup>*d*</sup> Conversion refers to fraction of starting material consumed in the reaction, <sup>e</sup> %H<sub>2</sub>O<sub>2</sub> efficiency = (moles of product formed/moles of H<sub>2</sub>O<sub>2</sub> reacted × 100. <sup>*f*</sup> Selectivity is the production rate of one component per production rate of another component, <sup>*g*</sup> Amount of metal atom in µmol present per 12.5 mg of catalyst. <sup>*h*</sup>TOF (turnover frequency) : Moles of

substrate converted per mole of active metal ion per hour. Bzald; Benzaldehyde, Styo: styrene oxide, Phetdiol: 1phenylethan-1,2-diol, Phacetal: phenyl acetaldehyde. Reaction condition: 25 mmol styrene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg catalyst, 6 ml of acetonitrile, 353 K, 18 h.

Catalyst	Cyclohexene	H <sub>2</sub> O <sub>2</sub>	Product s	TOF			
	conversion (%)	(%)	Allylic pro	oducts	Epoxidatio	(h <sup>-</sup> ')	
			Cyol	Cyone	Суох	Cydiol	
blank	02.6	25.5	28.9	09.1	55.6	06.2	-
1	03.8	21.9	34.2	14.5	35.4	15.9	-
2	03.1	16.7	36.4	13.4	39.5	10.7	-
3	85.6	87.0	34.5	41.2	12.3	12.0	42.65
4	71.4	71.4	38.3	42.2	11.2	08.4	41.75
5	97.5	97.5	31.6	49.8	13.3	05.3	50.78
6	81.9	92.8	33.3	46.3	10.6	09.8	48.69
NaY	05.4	45.1	13.7	15.7	31.6	38.8	-
FeY	21.3	28.0	21.3	23.5	34.5	20.7	238.1
RuY	19.4	23.8	26.3	29.5	31.2.	13.0	316.7
3Y	71.1	74.0	32.3	39.5	16.5	11.7	1208
4Y	64.0	64.0	31.3	39.4	19.8	09.6	970.8
5Y	84.4	84.4	27.4	46.7	21.8	4.1	2351
6Y	70.9	72.9	24.3	48.3	17.3	10.1	2255

**Table 6**. Oxidation of cyclohexene with 30% H<sub>2</sub>O<sub>2</sub> catalyzed 1-6, NaY, RuY, FeY, and 3Y-6Y at optimized reaction condition.

Cyol: 2-Cyclohexen-1-ol, Cyone: 2-Cyclohexen-1-one, Cyox: Cyclohexene oxide (1,2epoxycyclohexane), Cydiol:Cyclohexene-1,2-diol. TOF (turnover frequency): Moles of substrate converted per mole of active metal ion per hour. Reaction condition: 25 mmol cyclohexene, 25 mmol 30%  $H_2O_2$ , 12.5 mg catalyst, 6 ml of acetonitrile, 353 K, 18 h.

Catalyst	Limonene	H <sub>2</sub> O <sub>2</sub>	Product	TOF				
	conversion (%)	(%)	Allylic pr	oducts	Epoxidat	ion produc	ts	(h⁻')
	()		Col	Cone	Limox	Limdiox	Limgly	
blank	01.2	08.5	43.4	23.6	23.5	2.3	07.2	-
1	02.1	12.1	41.2	26.7	28.9	1.9	01.3	-
2	02.0	15.1	36.4	31.3	21.3	3.2	07.8	-
3	88.7	90.2	21.3	67.3	08.3	0.8	02.2	44.20
4	69.0	69.0	19.3	61.2	09.3	1.4	08.9	40.34
5	96.6	97.6	16.5	70.3	07.4	1.0	04.8	50.83
6	75.7	85.8	24.4	65.3	06.2	1.1	03.0	45.00
NaY	04.6	28.0	47.8	14.3	31.0	0.3	06.6	-
FeY	17.5	23.0	31.0	28.6	27.0	2.1	11.3	195.6
RuY	12.6	15.2	27.4	34.3	21.9	3.7	12.7	205.6
3Y	78.9	82.2	19.1	61.2	12.2	1.3	06.2	1341
4Y	67.8	67.8	14.3	69.7	10.8	0.8	04.8	1028
5Y	81.6	81.6	11.2	78.4	10.0	0.4	-	2273
6Y	55.5	57.1	14.3	81.3	03.1	-	01.3	1765

**Table 7**. Oxidation of limonene with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by 1-6, NaY, RuY, FeY, and 3Y-6Y at optimized reaction condition.

Col: Carveol, Cone: Carvone Limox: Limonene oxide, Limdiox: Limonene dioxide Limgly: Limonene glycol. TOF (turnover frequency): Moles of substrate converted per mole of active metal ion per hour. Reaction condition: 25 mmol limonene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg catalyst, 6 ml of acetonitrile, 353 K, 18 h.

Catalyst	α-pinene	$H_2O_2$	Product selectivity (%)						
	Conversion	efficiency	Allylic pr	oducts		Epoxidation		(h <sup>-1</sup> )	
	(		Vol	Vone	Mnol	Camal	Piox		
blank	01.0	7.1	31.5	35.3	08.1	03.9	21.2	-	
1	01.4	8.1	29.5	37.4	03.4	02.9	26.8	-	
2	02.1	11.3	32.9	30.7	14.3	11.4	10.7	-	
3	76.2	77.5	15.3	72.6	05.9	03.1	03.1	38.02	
4	54.4	54.4	17.3	69.3	06.4	01.3	05.7	31.75	
5	81.3	81.3	11.3	76.7	03.1	06.4	02.5	42.34	
6	64.5	73.1	16.3	71.6	02.9	02.4	06.8	38.34	
NaY	03.4	20.7	32.2	38.4	12.1	-	17.3	-	
FeY	16.9	22.2	35.3	51.3	02.0	-	11.4	188.9	
RuY	13.4	16.1	23.4	62.3	-	01.6	12.7	218.7	
3Y	69.6	72.8	13.3	71.8	04.5	03.0	07.4	1183	
4Y	56.8	56.8	15.4	67.9	03.8	06.9	06.0	816.6	
5Y	72.6	72.6	12.3	72.9	01.5	10.2	03.1	2023	
6Y	62.2	64.0	13.4	76.6	03.5	2.0	04.5	1978	
5Y <sup>R1</sup>	74.5	74.5	13.2	71.4	01.9	11.2	02.3	2006	
5Y <sup>R11</sup>	77.7	78.0	11.3	70.7	02.9	10.7	04.4	2057	
5Y <sup>R12</sup>	28.0	27.5	36.3	42.9	01.5	07.3	12.0	704.6	
5Y <sup>R3</sup>	75.9	75.9	10.3	69.9	05.8	11.5	02.5	-	
5Y <sup>R4</sup>	74.2	70.1	11.5	70.1	01.8	11.9	04.7	-	

**Table 8** Oxidation of  $\alpha$ -pinene with 30% H<sub>2</sub>O<sub>2</sub> catalyzed 1-6, NaY, RuY, FeY, and 3Y-6Y at optimized reaction condition.

Camal: Campholenal, Vol: Verbenol, Vone: Verbenone, Mnol: Myrtenol, Piox: Pinene oxide. 5Y<sup>R1</sup>: One time used catalyst 5Y which is dehydrated at 250 °C before second catalytic cycle. 5Y<sup>R11</sup>: One time used catalyst 5Y which is dehydrated at 350 °C before second catalytic cycle. 5Y<sup>R12</sup>: One time used catalyst 5Y which is dehydrated at 600 °C before second catalytic cycle. 5Y<sup>R3</sup>: Two times used catalyst 5Y which is dehydrated at 250 °C before third catalytic cycle. 5Y<sup>R4</sup>: Three times used catalyst 5Y which is dehydrated at 250 °C before third catalytic cycle. 5Y<sup>R4</sup>: Three times used catalyst 5Y which is dehydrated at 250 °C before fourth catalytic cycle. TOF (turnover frequency): Moles of

substrate converted per mole of active metal ion per hour. Reaction condition: 25 mmol  $\alpha$ -pinene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg catalyst, 6 ml of acetonitrile, 353 K, 18 h.

Catalyst	α-pinene Conversion (%)	Product	Product selectivity (%)							
		Vol	Vone	Mnol	Camal	Piox				
Fresh	100	3.5	20.7	5.8	35.9	34.1				
1 <sup>st</sup> run	81.3	5.8	20.0	3.5	31.5	39.2				
2 <sup>nd</sup> run	72.4	9.4	22.2	4.5	32.4	31.5				
3 <sup>rd</sup> run	58.3	7.5	18.4	6.0	30.5	37.6				

Table 9 Oxidation of  $\alpha$ -pinene with 30% H<sub>2</sub>O<sub>2</sub> catalyzed recycled catalyst 5Y.

Camal: Campholenal, Vol: Verbenol, Vone: Verbenone, Mnol: Myrtenol, Piox: Pinene oxide. Reaction condition: 25 mmol  $\alpha$ -pinene, 25 mmol 30% H<sub>2</sub>O<sub>2</sub>, 12.5 mg catalyst, 2.5 mmol H<sub>2</sub>SO<sub>4</sub>, 6 ml of acetonitrile, 353 K, 18 h.