List of Publication


Zeolite Y encaged Ru(III) and Fe(III) complexes for oxidation of styrene, cyclohexene, limonene, and α-pinene: An eye-catching impact of $\text{H}_2\text{SO}_4$ on product selectivity


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ABSTRACT

A novel Ru(III) and Fe(III) complexes of ligands 1 and/or 2 [where $1 = 2,2^{+}-(1\text{E},1\text{E})-(\text{azanediyl})$ bis(ethane-2,1-diy)]bis(azanlylidened)bis(methanlylidien)diphenol and $2 = 2,2^{+}-(1\text{E},1\text{E})-(\text{azanediyl})$ bis(ethane-2,1-diy)]bis(azanlylidened)bis(methanlylidien)diphenol] have been synthesized as 'neutral' and zeolite Y encapsulated complexes. These catalysts are characterized by various analytical tools such as FTIR, UV-vis, elemental analysis, ICP-AES, molar conductivity, $\text{H}$ and $\text{C}$ 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$^{-1}$), cyclohexene (Conv. 84.4%, TOF: 2351 h$^{-1}$), limonene (Conv. 81.6%, TOF: 2273 h$^{-1}$), and α-pinene (Conv. 72.6%, TOF: 2023 h$^{-1}$) oxidation with high selectivity of respective aliphatic products excluding the styrene oxidation, which undergoes epoxidation only. The addition of $\text{H}_2\text{SO}_4$ in an identical reaction catalyzed by 5Y not only surges 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 $\text{H}_2\text{SO}_4$ that facilitates the heterolytic $\text{O} \rightarrow \text{O}$ 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 amply drop in the activity and selectivity.

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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 oxoxygenation reactions 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 oxygen functionalization 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% $\text{H}_2\text{O}_2$ as an oxygen donor. Moreover, the identical reaction catalyzed by 5Y was carried out using 2.5 mmol $\text{H}_2\text{SO}_4$ as an additive to investigate the change in % conversion and selectivity of products. The detailed mechanistic study using UV–vis and the changes
A hierarchical zeolite-Y hampered metallo-ligand complexes for selective oxidation: A mechanistic point of view


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ABSTRACT

A series of Ni\(^{2+}\) and Mn\(^{2+}\) complexes with ligands 1 and 2 derived from the condensation of 1-(2-hydroxyphenyl)ethan-1-one and/or 1-(5-chloro-2-hydroxyphenyl)ethan-1-one with ethan-1,2-diamine have been synthesized as neat and zeolite Y enslaved complexes. The structures of these complexes were established on the basis of various physicochemical (XRD, ICP-AES, elemental analysis, BET, SEM, magnetic measurements, and TGA) and spectroscopic studies (UV−vis and FTIR). The catalytic performance of these hybrid materials was scrutinized for the oxidation of cyclohexene, phenol, styrene, and benzene using 30% H\(_2\)O\(_2\) as an oxidant. Among all catalysts, 3Y ably catalyzed the cyclohexene (100%), phenol (39.2%), styrene (99.3%), and benzene (20.7%) with the higher selectivity of Cyclohex-2-en-1-one (55.6%), catechol (73.2%), benzaldehyde (87.5%), and phenol (80.7%), respectively. It has been revealed that the presence of electron-withdrawing substituents on the aromatic ring of catalyst degrades the catalytic activity and the selectivity of products. The results show that the heterogeneous systems are easily salvaged and reused without substantial fall in the activity and selectivity. Moreover, the involvement of metal hydroperoxide during the catalytic reaction is confirmed by the preparation, characterization, and utilization of metal hydroperoxide of complex 4 as catalyst over phenol oxidation without oxidant.

1. Introduction

Oxidation reactions play an imperative role in many fields that benefit the chemical industries for the manufacture of high tonnage commodities, high-value fine chemicals, chemical intermediates and the pharmaceuticals [1–3]. Some selective oxidation processes, such as the conversion of benzene to phenol, phenol to catechol, styrene to benzaldehyde, and allylic oxyfunctionalization of cycloalkanes are the top most challenges of modern catalysis chemistry [4]. A significant uses of these oxyfunctionalized compounds such as aldehydes, alcohols, ketones, phenols, and epoxides devour a large amounts of energy in their production, usually catalyzed by non-recyclable mineral acids, expensive metal ions, and metal complexes, involve the usage of explosive, aggressive, and corrosive reagents and yield ample amounts of waste. The oxidation reaction that is significant in the manufacture of pharmaceutical and fine-

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Feature article

Zeolite-Y immobilized Metallo-ligand complexes: A novel heterogenous catalysts for selective oxidation


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Abstract

Transition metal [M = Co(II), Cu(II)] complexes of H3L1 and H4L2 ligands have been prepared as neat and nanohybrid zeolite-Y immobilized complexes. The various analytical tools such as FTIR, ICP-AES, elemental analysis, UV–vis, Brunauer, Emmett and Teller (BET) surface area analysis, Thermal analysis, scanning electron micrographs, Powder XRD, conductivity, magnetic moment, and AAS were employed for the characterization of the prepared catalysts. Among all catalysts, the [Cu(L1)]-Y (heterogeneous) and [Cu(L1)]-Y (homogeneous) have offered high activity and selectivity over oxidation of cyclohexene. Moreover, the [Cu(L1)] and [Cu(L1)]-Y were employed as catalyst over various organic substrates at identical reaction condition. The immobilized catalyst [Cu(L1)]-Y is found to be moderate active over oxidation of cyclohexene (75.2%), benzene (8.2%), phenol (14.5%), styrene (87.5%), benzyl alcohol (21.5%), limonene (11.2%), α-pinene (9.18%), and cyclooctane (76.8%) with high TON values (21942–2054). The mechanistic study using UV–vis and FTIR suggests the participation of active metalperoxo species, which is reinforced by its high catalytic activity over limonene (16.3%) in the absence oxidant.

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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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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. © 2016 Elsevier B.V. All rights reserved.

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-1-one) 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 KHSO4 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 cyclohexane-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 2-cyclohexen-1-one and 2-cyclohexen-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=MnIV, O=RuVIII 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.
Heterogeneous catalysts hold the edge over homogeneous systems: Zeolite-Y encapsulated complexes for Baeyer-Villiger oxidation of cyclohexanone

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Abstract

A series of heterogeneous catalysts [M(pamp)]-Y (Where, M = V, Mn, Fe or Cu; pamp = 2,2’-(1E,1’E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene)diphenol) was prepared by encapsulation of metal complexes within zeolite-Y. Synthesized materials were characterized by chemical, BET and thermogravimetric (TG) analysis, X-ray diffraction (XRD), UV–vis and infrared spectroscopies, and scanning electron microscopy (SEM). Zeolite-Y encapsulated complexes were tested in Baeyer-Villiger (B-V) oxidation of cyclohexanone beside neat complexes to check the aptitude of heterogeneous catalysts over the homogeneous system. The effect of experimental variables viz., solvents, catalysts amount, the mole ratio of substrate to an oxidant, temperature and reaction time on substrate conversion was also tested. Under the optimized reaction conditions, [VO(pamp)]=Y was found to be a potential candidate by providing 1500 TONs in cyclohexanone oxidation, and the selectivity towards 3-caprolactone was 85.2%.

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1. Introduction

The Baeyer-Villiger (B-V) oxidation, which could freely transform ketones to lactones or esters, is of marked synthetic value and has been extensively used in various syntheses of fine chemicals, pharmaceuticals and monomers for polymerization [1–7]. Usually, B-V oxidation with peracids, like trifluoroperacetic acid [8], perbenzoic acid [9] and m-chloro-perbenzoic acid [10] eventually produce large amount of waste. In last few years, a wide range of homogeneous metal complexes have been used for B-V oxidation [11–13] to improve reaction rate and selectivity, since their acid-base and redox properties can be tuned easily by simply changing ligand composition. However, homogeneous systems are often regarded as ill-defined with many limitations, including the decomposition and deactivation due to the formation of dimeric μ-oxo- and peroxo- bridged species, and separation problem as well.

On the other end, heterogeneous systems light up the catalysis field with sparkling rewards as catalyst separation from the homogeneous systems is typically stropisy. Plentiful efforts have been made to incorporate homogeneous Schiff base complexes on solid supports, such as anchoring metal complexes in a polymeric matrix [14], sulfonic acid-functionalized mesoporous SBA-15 [15], and encapsulation in zeolite cavities [16–19] have also been reported. In specific, encapsulation of metal complexes in the nanopores of zeolite-Y is an eye-catching eco-friendly technique for heterogenization; since no leaching is perceived when the complex is confined entirely in the nanocavities of zeolite-Y [20–23]. The as-prepared hybrid inorganic-organic material holds the number of heterogeneous catalysis feature over homogeneous catalysts in this context viz., shape selectivity, site isolation, better reactivity, withstand high temperatures, be prepared with the desired texture, be recycled, and be reused [24–28]. It has been prominent that the space constraints forced by the host framework can have a weakly impact on the geometry of the guest complex, which can induce changes in magnetic, spectroscopic and redox properties of the encapsulated complex, leading to a boosted activity and selectivity rather than its outlook in homogeneous account [29–31]. Zeolite-Y encapsulated complexes have been shown to be potential heterogeneous catalysts for numerous reaction processes viz., oxidation of alcohols [32], alkenes [33,34], alcohols [35,36], olefins [37], and...
The outlook of zeolite-Y hampered metal–ligand framework as heterogeneous catalysts: synthesis, spectral account and catalytic features

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Abstract Zeolite-Y enslaved complexes were prepared by the Flexible ligand method. Synthesized materials were characterized by various spectral tools like powder X-ray diffraction, spectral studies (UV–Vis and FT-IR), chemical analysis (ICP-OES and elemental), scanning electron microscopy, AAS and 1H-NMR techniques. Further, BET and thermogravimetric (TG) analysis were also done for characterization of surface area, pore volume, thermal behavior, and related parameters. Baeyer–Villiger oxidation of cyclohexanone was carried out over Zeolite-Y enslaved complexes using hydrogen peroxide (H2O2) as an oxidant. The performance of the heterogeneous system with the homogeneous system was compared to determine the protection effect of the zeolitic matrix over the active center on the catalytic properties. In addition, the effect of experimental variables (various solvents, amount of catalyst, the mole ratio of substrate and oxidant, temperature, and reaction time) was examined in order to get absolute reaction conditions. Under the optimized reaction conditions, [Fe(nbab)]2-Y was found to be a potential candidate, achieving 70 % \( \varepsilon \)-caprolactone selectivity.

Keywords Zeolite-Y · Metal–ligand framework · Heterogeneous catalyst · Cyclohexanone oxidation

1 Introduction

The Baeyer–Villiger (B–V) reaction is a significant oxidation process, providing a straight corridor to oxidize ketones to lactones or esters by organic peracids, and the lactones or esters are weighty industrial intermediates for the manufacture of polymers, pharmaceuticals, agrochemicals and herbicides [1–3]. Currently, the industrial process involves the use of \( m \)-chloroperoxybenzoic acid to produce \( \varepsilon \)-caprolactone by the oxidation of cyclohexanone [4]. However, peracids are pricey and possibly explosive, which restricts their use. Additionally, the acid by-product can reduce ester selectivity by unwanted side-reactions. Therefore, expansion of alternative oxidation methods is necessary which are commercially feasible. Conversely, catalysts are enforced for an active transfer of oxygen from the oxidant to the substrate when \( O_2 \) and aqueous \( H_2O_2 \) are used as oxidants. Aqueous \( H_2O_2 \) is a favorable oxidant for B–V reaction since the only by-product is water. Thus, the advance of catalytic B–V reaction using \( O_2 \) or aqueous \( H_2O_2 \) is essential, which satisfies the necessities of environmentally benign approaches, compared to outdated oxidation systems [5, 6].

Metal complex-catalyzed (homogeneous and heterogeneous) oxidation reactions are important reactions in chemical industry [7, 8]. The major downside of homogeneous metal complexes as catalysts is their irreversible deactivation due to the formation of \( \mu \)-oxo and \( \mu \)-peroxo dimeric and other polymeric species, especially when using oxidant [9]. Nanoporous materials such as framework silicates, zeolites, carbon nanotubes and nanoporous silicon have been used to iron out the kinks of homogeneous systems [10]. During the last years, there have been extreme developments in synthesis, characterization, and application of novel nanoporous materials [11, 12].
Synthesis, spectral investigation and catalytic aspects of entrapped VO(IV) and Cu(II) complexes into the supercages of zeolite-Y

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HIGHLIGHTS

- We have synthesized VO(IV) and/or Cu(II) based neat and their entrapped complexes into the supercages of zeolite-Y.
- The comparative spectroscopic, thermal, morphological and crystalline properties of these complexes were achieved.
- Their catalytic activities were tested over oxidation of limonene reaction using 30% H2O2 as oxidizing agent.
- Among them [VO(\(\text{L}_2\text{O}\)]-Y catalyst shows higher catalytic activity with limonene glycol selectivity.

GRAPHICAL ABSTRACT

ABSTRACT

VO(IV) and Cu(II) complexes with Schiff base ligand derived from 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5-one (PMFP) and 2-amino phenol have been synthesized as their neat and entrapped complexes into the supercages of zeolite-Y. The compounds were characterized by chemical analysis (ICP-OES and elemental), electronic and/or UV reflectance spectra, FTIR spectroscopy, X-ray powder diffraction patterns, SEMs, BET and thermogravimetric (TG) analysis. All the prepared catalysts were tested on the liquid phase limonene oxidation reaction, using 30% H2O2 as an oxidant. Limonene glycol, carveol, carveone and limonene 1,2-epoxide were the main products obtained. It was observed that zeolite-Y entrapped complexes exhibited higher catalytic activity than neat complexes. The catalysts undergo no metal leaching and can be easily recovered and reused. The use of inexpensive catalyst and oxidant are significant practical advantages of this environmentally friendly process.

Keywords:
Zeolite-Y entrapped complexes
Schiff base ligand
Oxidation of limonene

Introduction

Transition metal complexes are effective and selective catalysts in a variety of organic reactions [1–3]. Although these catalysts offer interesting results, such as low influence of diffusion mechanisms on reaction performance; they become more useful if the separation process is targeted to recover them at the end of reaction especially for precious and strategic metal catalysts. However, the inclusion of separation process in some cases might be very difficult and challenging.

The current developments in catalysis are mainly focused on entrapment of metal complexes either on inert materials, or on
Catalytic oxidation of limonene over zeolite-Y entrapped oxovanadium (IV) complexes as heterogeneous catalysts

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ABSTRACT

A series of VO(IV) complexes with Schiff base ligands derived from vanillin thiophene-2-carboxylic hydrazide (VTCH), vanillin furonic-2-carboxylic hydrazide (VFCH), salicylaldehyde thiophene-2-carboxylic hydrazide (H 2 STCH) and/or salicylaldehyde furonic-2-carboxylic hydrazide (H 2 SFCH) have been synthesized as neat and their entrapped complexes into the nanopores of zeolite-Y. These materials were characterized by several techniques: chemical analysis (ICP-OES and elemental) and spectroscopic methods (FT-IR, electronic, XRD, SEMs and BET). All the prepared catalysts were tested over the liquid phase limonene oxidation reaction, using tert-butyl hydroperoxide (TBHP) and/or 30% H 2 O 2 as oxidants. Limonene glycol, carveol and carveone were the main products obtained. It was observed that zeolite-Y-based entrapped complexes exhibited higher catalytic activity than neat VO(IV) complexes. These zeolite-Y based entrapped complexes are stable and recyclable under current reaction conditions. Amongst them, [VO(VTCH) 3 ]-Y showed higher catalytic activity (97.7%) with limonene glycol (45.1%), selectivity.

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1. Introduction

Recent progresses of vanadium complexes in catalytic and medicinal properties have enthused their design and synthesis [1]. The coordination chemistry of oxovanadium (IV) and oxovanadium (V) is experiencing a frank development with significance in the fields of biological, medicinal, material and synthetic chemistries [2–6]. Especially, the use of vanadium complexes in oxidation catalysis is of particular synthetic interest, namely directed toward organic synthesis. Indeed, this metal displays easily inter convertible different oxidation states, readily accessible high oxidation states, a variety of coordination numbers, a high affinity for oxygen and can behave as a Lewis acid, characteristics that can help its application in redox and Lewis acid catalyzed or promoted reactions [7].

Limonene is the main component of citrus oil being easily obtained from the fruit peel waste. Its derivatives functionalized with oxygen are important intermediates in the synthesis of perfumes, pharmaceuticals, food additives and agrochemicals [8,9]. Epoxides will be the selective products if oxidation occurs at olefinic positions. If the oxidation takes place at allylic positions, the major products will be carveol and carveone, even though a large number of other products may also be formed. In addition, limonene has two olefinic bonds (1, 2 and 8, 9) and the oxidation can take place at either or both of these sites. Allylic oxidation takes place usually via a free radical chain reaction pathway; it generally occurs when the intermediate metallic species are in a low oxidation state [9]. On the other hand, epoxide formation is more likely to occur when oxometallic species are in a high oxidation state, such as O = Mn IV, O = Ru VIII [10]. However, both mechanisms may occur simultaneously, since other variables than the nature of the metallic species (e.g. the stability of the radicals formed), must be taken into account. In acidic reaction media, the limonene oxide may be hydrolyzed forming limonene glycol [11–13].

Generally, limonene is epoxidized via homogenous stoichiometric peracid route [14]. However, this route is not environmentally benign and consequently, it becomes increasingly unacceptable. In addition, Schiff base complexes in particular Metal(Salen) complexes are often described as good epoxidation catalysts, due to their high activity and selectivity [15,16]. However, they might be easily deactivated, in homogeneous liquid solution, due to the formation of μ-oxo dimers and other polymeric species [17,18]. Catalyst separation from the homogeneous liquid solution is also usually troublesome. Numerous attempts have been
RESEARCH LETTER

Zeolite-Y entrapped bivalent transition metal complexes as hybrid nanocatalysts: density functional theory investigation and catalytic aspects


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The intriguing research toward the exploitation of zeolite-Y-based hybrid nanocatalysts for catalytic oxidation reactions has been growing significantly. In the present investigation, we describe the synthesis of zeolite-Y entrapped transition metal complexes of the general formulae $[\text{M(SFCH)}_x\text{H}_y\text{O}]^{-}\text{Y}$ (where, $\text{M} = \text{Mn, Fe, Co, Ni} (x = 3)$ and $\text{Cu} (x = 1)$; $\text{H}_2\text{SFCH} = \text{(E)}\text{N}^\text{+}-\text{(2-hydroxybenzylidene)}\text{furan-2-carboxhydrizide)}$. These nanocatalysts have been characterized by various physicochemical techniques. Density functional theory calculations are performed to address the relaxed geometry, bond angle, bond length, dihedral angle, highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) energy gap, and electronic density of states of $\text{H}_2\text{SFCH}$ ligand and their next transition metal complexes. The observed HOMO–LUMO gap and the Fermi energy is higher for $\text{Cu(II)}$ complexes, which demonstrates the better catalytic activity of this nanocatalyst. The catalytic activity was performed in liquid-phase oxidation of cyclohexane using hydrogen peroxide as oxidant to give cyclohexanone (CyONE) and cyclohexanol (CyOL). Among them, $[\text{Cu(SFCH)}_3\text{H}_2\text{O}]^{-}\text{Y}$ catalyst has the highest selectivity toward CyONE (84.5%).

Keywords: Zeolite-Y; hybrid nanocatalysts; cyclohexane oxidation; DFT

1. Introduction

The selective oxidation is an industrially momentous reaction for the synthesis of chemical intermediates in the manufacture of high tonnage commodities, high-value fine chemicals, and pharmaceutically important ingredients but still is an ineffective process. The heterogeneous catalysts offer great advantages such as effortless separation of product, catalyst revival, and make it suitable for continuous processing. As a result, heterogenization of homogeneous catalysts has become a significant approach for obtaining supported catalysts that sustain the active catalytic sites of the homogeneous analog (1, 2). The encapsulation of the transition metal complexes inside the nanopores of zeolite is one of the heterogenization methods and also is a theme of contemporary research (3–7). Heterogenization is accomplished either by entrapping the metal complex within the zeolite nanocavities or by anchoring and/or tethering them to inert supports (8). The structural design of zeolite-Y-based hybrid nanocatalysts via flexible ligand approach is convenient and ideal because the complex, once formed inside the cages of the zeolite is fitted suitably and not easily to diffuse out during the catalytic reaction (9, 10).

In particular, the selective oxidation of cyclohexane is an industrially important chemical reaction because of its oxidized products, such as cyclohexanol (CyOL) and cyclohexanone (CyONE), which are important intermediates in the production of adipic acid and caprolactam. Caprolactam is used in the manufacture of Nylony-6 and Nylony-66 polymers. In a recent industrial process, cyclohexane is oxidized at a temperature range of 150–170°C and pressure of 115–175 psi in the presence of homogeneous cobalt salt, where the conversion is very less (~4%), and the process is environmentally hazardous (11, 12). With the emphasis on environmentally benign catalytic oxidation of cyclohexane, several research groups have been designing various catalytic systems (13–20).

The use of computational techniques in catalysis, homogeneous as well as heterogeneous, has become explored mainly because of the sophistication of

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1. **Poster presented** on 8th and 9th January 2016 in chemical sciences in present scenario (CSIPS-2016) at V.P and R.T.P. Science College, Vallabh Vidyanagar, Gujarat, India.


3. **Poster presented** on “catalytic oxidation of cyclohexene Catalyzed by ship in bottle complexes” in ISCBC on 25th to 28th February 2015 at central drug research institute, Lucknow, U.P, India.

4. **Poster presented** on “synthesis, characterization and catalytic performance of transition metal complexes dispersed within nanopores of zeolite-Y” on 5th and 6th January 2015 in International conference on Nanomaterials for sustainable green technology at K.V. Pendhalkar college, Dombivali, Maharashtra, India.

5. **Oral presentation** on “catalytic oxidation of phenol over zeolite-Y entrapped Mn(III) complexes as heterogeneous catalyst” on 23rd and 24th October 2013 in National conference on frontier areas in chemistry and workshop on quantum mechanics and research methodology at Shri Shivaji science college, Amravati, Maharashtra, India.

6. Workshop attended on 23rd and 24th October 2013 in National conference on frontier areas in chemistry and workshop on quantum mechanics and research methodology at Shri Shivaji science college, Amravati, Maharashtra, India.

7. National seminar attended on advances in polymer synthesis for new materials on 19th October 2013 at Applied chemistry Department, Vadodara, Gujarat, India.
Certificate

This is to certify that Prof./Dr./Mr./Ms. Harish D. Nakum has attended National Seminar entitled "Chemical Sciences In Present Scenario (CSIPS - 2016)" organized by Chemistry & Industrial Chemistry Departments of V. P. & R. P. T. P. Science College, Vallabh Vidyanagar held on 8-9th January, 2016.

He/She has participated in Oral/Poster presentation.

Dr. Bhavesh Patel
Convener & Principal

Dr. B. C. Dixit
Coordinator

Dr. V. K. Sinha
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Dr. K. D. Patel
Organizing Secretary
Certificate of Presentation

This is to certify that, Mr./Ms./Dr. M. K. Dhamne, University of Pune, has participated and presented a paper entitled "Oxidation of Ethylene" in the oral/poster session of "11th Annual Session of Students' Chemical Engineering Congress, SCHEMCON-2015" during 12th & 13th September 2015 at Department of Chemical Engineering, MIT Academy of Engineering, Alandi (D), Pune-412105, Maharashtra.

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This is to certify that

Harendra D. Nakum has actively participated in the 21st ISCB International Conference (ISCB-2015) jointly organized by Indian Society of Chemists and Biologists and CDRI, Lucknow, India during February 25-28, 2015. He/She has presented a paper in the ISCB-2015 and presented a plenary talk/presentation.

P. M. S. Chauhan
Organizing Secretary
ISCB-2015

Central Drug Research Institute, Lucknow, U.P. India
Certificate

This is to certify that

Mr. Haresh D. Nakum

of Department of Chemistry, M. K. Bhavnagar University,

Bhavnagar, Gujarat has participated & presented poster in Two Day International Conference on Nanomaterials for Sustainable Green Technology

January 5 & 6, 2015

K. V. Pendharkar College, Dombivli

K. V. Pendharkar College

Dombivli Shikshan Prasarak Mandal's

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Departments of Chemistry & Physics

UNIVERSITY OF MUMBAI

International Conference On Nanomaterials for Sustainable Green Technology

At

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(Domivli)

Dr. Bholanath T. Mukherjee

(Principal)

Dr. Anuradha K. Ranade

(Convener)

Dr. Kailash R. Jagdeo

(Organizing Secretary)
This is to certify that Prof./Dr./Mr./Mrs./Ms. Haresh Nakum (Research Student) of Catalysis Division, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar, Gujarat has participated in the National Conference on Frontier Areas in Chemistry held at Dept. of Chemistry, Shri Shivaji Science College, Amravati on 23rd & 24th October, 2013 and oral presentation on "Catalytic oxidation of phenol over zeolite-Y entrapped Mn(III) complexes as heterogeneous catalysts"
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Certificate

This is to certify that, Prof./Dr./Mr./Mrs./Ms. Haresh Nakum
of Catalysis Division, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar, Gujarat
has attended Workshop on Quantum Mechanics and Research Methodology held at
Dept. of Chemistry, Shri Shivaji Science College, Amravati on 25th October, 2013.

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Shri Shivaji Science College, Amravati
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This is to certify that Mr. / Ms. / Dr. Naresh has attended the National Seminar on "Advances in Polymer Synthesis for New Materials" held on 19th October, 2013.

Prof. P. T. Deota
Head
Certificate

This is to certify that

Mr. Haresh D. Nakum
of M. K. Bhavnagar University, Bhavnagar, Gujarat, India
has presented poster on Synthesis, characterization and catalytic performance of transition metal complexes dispersed within nanopores of zeolite-Y and awarded 1st prize,
in Two Day International Conference on Nanomaterials for Sustainable Green Technology

January 5 & 6, 2015
At
K. V. Pendharkar college, Dombivli.

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(Organizing Secretary)

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