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Fe₃O₄@dopa (dopa = dopamine hydrochloride) functionalized Mn(III) Schiff base complex: A promising magnetically separable heterogeneous catalyst for oxidative transformations

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ABSTRACT

A chiral Schiff base complex has been prepared by treating (R)-1,2-diaminopropane with 3,5-dichlorosalicylaldehyde in ethanol, followed by addition of manganese chloride hexahydrate to generate a homogeneous catalyst, [MnL(Cl)(H₂O)] (HMN). Crystal structure of the complex reveals its mononuclear nature. Circular dichroism (CD) studies indicate that the ligand and its corresponding complex contain an asymmetric center. The catalytic activity of HMN toward epoxidation of alkenes, oxidation of alcohols and oxidation of alkanes has been investigated in the presence of iodosylbenzenediacetate (PhI(OAc)₂), in acetonitrile. In the present work we found yields to be much higher compared to our previous approaches. For further adaptation, we attached our efficient homogeneous catalyst with surface modified magnetic nanoparticles (Fe₃O₄@dopa) and thereby obtained a new magnetically separable nanocatalyst Fe₃O₄@ dopa@MnLCl (FDM). This catalyst has been characterized and its oxidation ability assessed in similar conditions as those used for the homogeneous catalyst. Enantiomeric excess in epoxide yield reveals retention of chirality of the active site of Fe₃O₄@dopa@MnLCl. The catalyst can be recovered by magnetic separation and recycled several times without significant loss of catalytic activity.



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1. Introduction

Research in the field of catalysis mainly focused on augmenting catalytic activity and selectivity. Recovery of the catalyst was not a serious issue. But for "green chemistry" of catalytic reactions, the recovery and reuse of catalysts emerges as an important factor [1-6]. Magnetically separable nanocatalysts are an emergent topic of research [7–9] especially when these magnetically separable nanocatalysts are tuned with metal complexes [10,11]. Magnetically separable nanoparticles have excellent catalytic activity mainly due to their higher surface area, appreciable mechanical stability, increasing contact between catalyst and reactants, and also good dispersion in a reaction mixture. Magnetic nanoparticles have advantages, such as insolubility in reaction mixture, paramagnetic nature, and facile separation of the nanocatalyst at the end of the reaction by simply using a magnet thus avoiding catalyst filtration. Also these nanoparticles resist aggregation of nanocatalyst which increases the durability of the catalysts, recycling, and reusability [12]. Much effort has been expended for synthesis of magnetic separable nanoparticles and their applications in catalysis [13–15]. Current research focuses on greener synthesis of nanoparticles and their applications [16]. The use of nanoparticles as catalysts in organic transformations provide high surface areato-volume ratios [17, 18]. Homogeneous units anchored on nanoparticle supports heightens catalytic activity since the overall system still behaves as if dissolved in a solution. The choice of nanoparticles can also deliver additional functionality into the catalytic system [19]. Synthesis of iron oxide nanoparticles is cost effective coupled with simple synthetic approaches, and since suitable ligands can easily be anchored on their surface [20-23], they offer excellent potential as a catalyst support. Mn(III) complexes with Schiff-base ligands displaying N₂O₂ coordination have been reported as soluble and efficient catalysts in olefin epoxidations [24-27]. In our recent work we illustrated the epoxidation capability by various manganese and iron Schiff base complexes [28, 29]. Earlier we had explored only epoxidation capability by our synthesized catalyst. In the present work we report the synthesis of a new magnetically separable nanocatalyst, Fe₃O₄@dopa@MnLCl (FDM). Our previous efforts to explore the oxidation capabilities of our synthesized MSNps were futile hence in our present approach the main motive was to explore the versatility of our synthesized nanocatalyst. The ligand backbone of our catalyst in the present work is similar to our previously reported work [28]. We employ poorly explored oxidizing agent iodosobenzene diacetate (PhI(OAc)₂). PhI(OAc)₂, a precursor toward synthesis of PhIO, is highly soluble in most organic solvents, easy to handle and also commercially available thus making it a suitable candidate for various oxidation reactions [30]. Here we alter the metal center as shown in Scheme 1. Altering the metal center provides comparatively greater yield compared to previous catalyst and hence subjected it to various organic transformations such as epoxidation, alcohol oxidation and alkane oxidation; besides alkene epoxidation our catalyst was very effective in oxidizing alcohols and alkanes. Our synthesized nanocatalyst was easily recovered and reused for more than five times without any loss of catalytic activity or selectivity.

2. Experimental

2.1. Physical methods and materials

All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use.



Scheme 1. Schematic diagram for the formation of [MnL(Cl)(H₂O)].

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra (4000–500 cm⁻¹) were recorded at 27 °C using a Perkin-Elmer RXI FT-IR spectrophotometer with KBr pellets. Electronic spectra (800–200 nm) were obtained at 27 °C using a Shimadzu UV-3101PC with methanol as solvent and reference. Thermal analyses (TG-DTA) were carried out on a Mettler Toledo (TGA/SDTA851) thermal analyzer in flowing dinitrogen (flow rate: 30 cm³ min⁻¹). Field Emission Scanning Electron Microscope (FE-SEM) measurements were carried out with a JEOL JSM-6700F field-emission microscope. Transmission Electron Microscope (TEM) measurements were carried out with a JEOL (Japan) JEM2100 high-resolution transmission electron microscope, X-ray powder diffraction (XRPD) was performed on a XPERT-PRO diffractometer with monochromated Cu-Kα radiation (40.0 kV, 30.0 mA) at room temperature. A vibrating sample magnetometer (EV-9, Microsense, ADE) was utilized for obtaining the magnetization curves. The ¹H NMR spectra were recorded on a Bruker AC300 spectrometer. CD spectra were measured with a Jobin Ivon CD 6 spectrophotometer. Conductance of methanolic solutions of complexes were measured using a SYSTRONICS 306 conductivity meter. A vibrating sample magnetometer (EV-9, Microsense, ADE) was utilized for obtaining magnetization curves. Thermo Scientific iCAP 7400 ICP-OES was utilized for detection of leaching of manganese ions from the catalyst.

2.2. Syntheses of [MnL(Cl)(H,O)] (HMN)

Ethanolic solution (10 mL) of (R)-1,2-diaminopropane (0.74 g, 1 mmol) was added slowly to 20 mL ethanolic solution of 3,5-dichlorosalicylaldehyde (0.382 g, 2 mmol). Immediate precipitation of HL took place. Ethanolic solution (10 mL) of manganese chloride hexahydrate (0.135 g, 0.5 mmol) was added to the suspension of HL. Yellow precipitate of HL disappeared readily to give a deep brown solution. The solution was stirred overnight. Black micro crystals were formed from DMF after a few days. Yield: 90% (with respect to L). Anal. calcd for **HMN**: C, 38.78; H, 2.68; N, 5.32. Found: C, 37.55; H, 2.27; N, 5.49. IR (KBr): v(C=N) 1614.63 cm⁻¹; v (skeletal vibration) 1527.40 cm⁻¹; UV/vis (CH₃CN): $\lambda_{max/nm} = 272$, $\lambda_{max/nm} = 377$.

2.3. Synthesis of Fe_3O_4NPs

Preparation of magnetic nanoparticles Fe₃O₄ have been done following identical procedure as reported earlier by Varma *et al.* [31].

2.4. Synthesis of Fe₃O₄@dopa

Fe₃O₄@dopa has been prepared by following similar method as mentioned previously [31].

2.5. Synthesis of Fe₃O₄@dopa@MnLCl (FDM)

Fe₃O₄@dopa@MnLCl has been synthesized by following similar procedure as we reported [28, 29]. IR (KBr): v(C=N) 1648 cm⁻¹; v (skeletal vibration) 1527, 1486 cm⁻¹; v (Fe₃O₄) 631 cm⁻¹.

2.6. Catalytic oxidation of organic compounds

We investigated catalytic activity of our synthesized homogeneous complex MnL(Cl)(H₂O) for oxidation of alkenes, alcohols and alkanes. The details of the reactions are described below.

2.6.1. Control experiment

To inspect the capability of PhI(OAc)₂ to oxidize directly without any catalyst, control experiments were performed taking substrate and PhI(OAc)₂ only. A solution of substrate (1 mmol) and PhI(OAc)₂ (1.5 mmol) was taken in acetonitrile and stirred magnetically until reaction was complete. Upon completion, diethyl ether was used to extract the organic products (4 mL × 3) and ¹H-NMR analysis was performed. Extreme low conversion (< 5%) was found at the end of the analysis.

2.6.2. Catalytic oxidation by [MnL(Cl)(H₂O)]

The homogeneous catalyst (0.01 mmol) was suspended in solution of substrates (1 mmol) in CH_3CN (5 ml). Then the mixture was allowed to equilibrate at 60 °C. We added different amounts of $PhI(OAc)_2$ (as illustrated in footnote of each table) in the mixture with stirring. The stirring was continued for five hours at 60 °C in air. Upon completion diethyl ether was used to extract the organic products and ¹H-NMR analysis was performed.

2.6.3. Catalytic oxidation by Fe₃O₄@dopa@MnLCI (FDM)

 $Fe_3O_4@dopa@MnLCI (FDM) (0.01 g)$ was suspended in solution of substrates (1 mmol) in $CH_3CN (5 ml)$. Then the mixture was allowed to equilibrate at a reaction temperature of 60 °C. We added different amounts of $Phl(OAc)_2$ (as illustrated in footnote of each table) in the mixture with stirring. The stirring was continued for five hours at 60 °C in air. The catalyst particles were then collected with a magnet at the bottom of the reaction vessel followed by careful decantation of the supernatant liquid. The reaction mixture was worked up following the general procedure as mentioned in the previous section and ¹H-NMR analysis was performed.

2.6.4. Characterization and reusability Fe₃O₄@dopa@MnLCl

We have also assessed the recyclability of our synthesized catalyst. A series of experiments were carried out by performing oxidation of benzyl alcohol, epoxidation of (*E*)-stilbene and oxidation of diphenylmethane catalyzed by $Fe_3O_4@dopa@MnLCl$ nanocatalysts to examine their activity after five runs. After each run the catalysts were reclaimed by application of a magnet. Then these catalysts were washed with deionized water and acetonitrile to remove any absorbed products followed by drying. From the oxidation results it is evident **FDM** can be recovered and reused several times without loss in conversion and yield as shown in Table 1. The used catalysts were characterized by TEM and FTIR. The results indicate the catalysts are stable with efficient activity in all the reaction runs (Table 1). We did not find any leaching of manganese ions into solution from ICP-OES analysis.

2.7. X-ray crystallography

Intensities data for crystal structure analysis of **HMN** were collected on a Bruker Smart Apex diffractometer equipped with a CCD. In all cases measurements were conducted at room temperature with Mo-K α radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing, and scaling of the data sets were performed using Bruker Smart Apex and Bruker Saint packages [32]. The structure was solved by direct methods and subsequent Fourier analyses [33] and refined by full-matrix least-squares method based on F² with all observed reflections [34]. Hydrogens were placed at calculated positions and included in final cycles of refinement. All calculations were performed using the WinGX System, Ver 1.80.05 [35], PLATON99 [36] and ORTEP3 [37] programs. Crystal data and details of refinements are given in Table 2.

3. Results and discussion

3.1. Synthesis, rationalization, and characterization of the homogeneous catalyst

HL was prepared by reacting 3,5-dichlorosalicylaldehyde with (R)-1,2-diaminopropane in ethanol. HL was treated with $MnCl_2 GH_2O$ to generate the Schiff base complex. X-ray diffractible single crystals were obtained after a few days. **HMN** was characterized using regular physicochemical techniques. IR band at 1623 cm⁻¹ can be assigned to the C=N of azomethine present in the complex and bands at 1529 and 1431 cm⁻¹ indicate skeletal vibrations of aromatic moiety (Figure S1). The appearance of a broad absorption at 3000 cm⁻¹ for the

Table 1. Catalytic oxidation of alcohols, alkanes, and epoxidation of alkenes in CH_3CN by $Phl(OAc)_2$ using $Fe_3O_4@dopa@MnLCI$ (**FDM**) as the catalyst (reused up to five times).

		Conversion ^a (% per cycle)			Yield ^b (% per cycle)						
Entry	Substrate	1	2	3	4	5	1	2	3	4	5
1	Benzyl alcohol	90	88	87	83	78	94	90	88	85	80
2	Diphenylmethane	87	84	80	78	75	92	90	87	85	78
3	(E)-Stilbene	94	90	87	79	82	90	87	84	80	76

Notes: Reaction conditions:

^aCatalyst (40 mg), substrate (2 mmol), Phl(OAc)₂ (2 mmol), CH₃CN (10 mL) were stirred at room temperature for 4 h. ^bIsolated yield.

Empirical formula	C17HCI.MnN.O.
Formula weight	526.49
Crystal system	Orthorhombic
Space group	Aba2
<i>a</i> (Å)	13.339(5)
b (Å)	13.611(4)
<i>c</i> (Å)	21.822(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	3962(2)
Ζ	8
$D_{\rm calc}$ (g/cm ⁻³)	1.765
μ (mm)	1.363
F(000)	2112
heta range	1.9–20.8
Total data	5830
Unique data	2056
R _{int}	0.047
Observed data ($l > 2\sigma(l)$)	1252
Radiation (Å)	0.71073
Parameters	250
R ₁ ^a	0.0535
$\dot{WR}_{2}(l > 2\sigma(l))^{a}$	0.1853
GOF on F ²	1.004
Residuals (e Å ⁻³)	-0.41, 0.72

Table 2. Crystal data and structure refinement details for [Mn(L)(Cl)(H₂O)].

complex indicates the presence of coordinated water. The bonding of the Schiff base ligand to manganese(III) is shown by bands at 500–400 cm⁻¹ in the spectra of the complex from (Mn–O) and (Mn–N) stretches (Figure S1). Electronic absorption spectra of the complex (Figure S2) showed multiple bands in the UV and visible regions. Absorption maxima observed in the near-UV regions (below 300 nm) are due to π – π * transitions involving the phenolate units. Bands between 300 and 350 nm can be attributed to charge transfer transitions from the out-of-plane p π orbital (HOMO) of the phenolate oxygen to the half-filled d_{x2-y2}/d_{z2} orbital of high spin manganese(III). The lowest energy bands (around 400 nm) are proposed to arise from charge-transfer transitions from the in-plane pp orbital of the phenolate to the half-filled dp* orbital of manganese(III) [38, 39]. Molar conductance of the complex in acetonitrile was 2.2 Ω ⁻¹ cm² M⁻¹, implying that the complex is a non-electrolyte. Circular dichroism (CD) measurements for the ligand and its corresponding complex are presented in Figure 1. The CD spectrum for [MnL(CI)(H₂O)] is the reverse of HL, suggesting inversion of configuration after complexation.

3.2. Description of crystal structure of HMN

The X-ray structure of **HMN** is illustrated in Figure 2. Selected bond lengths and angles are listed in Table 3. According to the X-ray structure the Schiff base ligand coordinates tetradentate to a single manganese. The metal center is six-coordinate. The two phenolic oxygens and the two imine nitrogens of the Schiff-base constitute the basal plane and a single chloride and a single water occupy the two axial positions. Two Mn–O (phenolic) bonds have similar bond distances, 1.861(4) and 1.899(4) Å, respectively. The Mn–N (imine) distances of 1.91(3) and 2.08(4) Å are also comparable, whereas Mn–Cl bond distance is 2.481(5) Å.



Figure 1. Circular dichroism (CD) spectra of the chiral ligand (HL) and the chiral complex [MnL(Cl)(H₂O)].



Figure 2. ORTEP drawing (ellipsoid probability at 30%) of [MnL(Cl)(H₂O)].

Table 3. Selected bond lengths (Å) and angles (°) for [MnL(Cl)(H₂O)].

		2	
Mn-01	1.93(3)	Cl5-Mn-O1	99.6(8)
Mn-O2	1.88(3)	Cl5–Mn–O2	94.2(8)
Mn–Cl5	2.481(5)	Cl5–Mn–O1w	173.4(4)
Mn–N1	1.91(3)	CI5–Mn–N1	89.9(8)
Mn–N2	2.08(4)	CI5–Mn–N2	88.6(12)
Mn-01w	2.302(10)	01-Mn-01w	85.9(9)
		01-Mn-02	93.4(11)
		O1-Mn-N1	93.4(13)
		O1-Mn-N2	170.0(13)
		01w-Mn-02	89.1(10)
		O1w-Mn-N1	86.1(9)
		O1w-Mn-N2	85.5(13)
		O2-Mn-N1	171.3(12)
		O2-Mn-N2	91.6(13)
		N1–Mn–N2	80.9(14)



Scheme 2. Schematic representation of the preparation of Fe₃O₄@dopa@MnLCl particles.

3.3. Preparation and characterization of Fe₃O₄@dopa@MnLCl

Preparation of magnetically separable nanoparticles is given in Scheme 2. Synthesis and characterization of Fe₃O₄ and Fe₃O₄@dopa have been performed by following methods reported earlier [28, 29]. First step in the preparation of magnetically separable nanocatalyst involves synthesis of Fe₃O₄ nanoparticles by co-precipitation method followed by condensation with dopamine hydrochloride to generate Fe₃O₄@dopa. Last step in Scheme 2 involves functionalization of Fe₃O₄@dopa by [MnL(Cl)(H₂O)]. [MnL(Cl)(H₂O)] (1 g) was added to a dispersed acetonitrile solution of amine-functionalized nano-Fe₂O₄ (Fe₂O₄@dopa, 500 mg) followed by stirring the mixture for 14 h at room temperature. The product was allowed to settle and then washed several times with acetonitrile and dried under vacuum at 50 °C for 3 h. The amount of immobilized manganese complex was determined by the Persulfate-Arsenite method [40]. The manganese content was 0.1 mmol q^{-1} of the supported catalyst. FTIR spectra of Fe₃O₄@dopa@MnLCl were observed at 583 and 629 cm⁻¹ which are the signature absorptions of Fe-O bonds, confirming the presence of iron oxide (Figure S3) [28, 29]. Dopamine incorporation is confirmed by the presence of a peak at 1479 cm⁻¹ which can be credited to the vibration of the benzene ring present in dopamine moiety. Several new peaks are generated for Fe₃O₄@dopa@MnLCl, along with the characteristic peak of Fe₂O₄. The peak at 1516 cm⁻¹ may be assigned as the skeleton vibration of the complex; the prominent peak at 1647 cm⁻¹ may be due to C=N vibration of incorporated complex moiety. From FTIR spectra we conclude that the desired surface modification of MNPs has been done. The degree of crystallinity of magnetic Fe₃O₄, Fe₃O₄@dopa with the help of PXRD has already been reported in our previous endeavors [28, 29]. The PXRD pattern of our synthesized magnetically separable nanocatalyst Fe₃O₄@dopa@MnLCl is consistent with the



Figure 3. TEM image of Fe₃O₄@dopa@MnLCl.

standard $Fe_{3}O_{4}$ sample (Figure S4). The average particle size of **FDM** nanoparticles were estimated from the Scherrer equation [41]:

$$d = \frac{k\lambda}{B\cos\theta} \frac{180^{\circ}}{\pi}$$

where d denotes the main crystallite diameter, k (0.89) represents the Scherrer constant, λ the X-ray wavelength and B is the full width half maximum (FWHM) of **FDM** diffraction peak. The average nanoparticle size is 10–14 nm. The same peaks are observed among the Fe₃O₄@ dopa and Fe₃O₄@dopa@MnLCl in PXRD patterns, indicating that the resultant nanoparticles contain pure Fe₃O₄ with a spinel structure and that the process of grafting did not instigate any phase change of Fe₃O₄ as previously found by our group for similar systems [28, 29]. For further reassurance of the surface modification of magnetic Fe₃O₄ and incorporation of MnLCl on the surface of Fe₃O₄@dopa, thermogravimetric analysis (TGA) is carried out (Figure S5). TGA results suggest that the augmented weight loss is due to increasing amount of attached organic moiety from Fe₃O₄@dopa to Fe₃O₄@dopa@MnLCl. These results are consistent with those reported earlier by our group [28, 29]. Scanning electron microscopy (SEM) image of Fe₃O₄@dopa@MnLCl in Figure S6 depicts morphologies which are quite different from those of Fe₃O₄NPs and Fe₃O₄@dopa that we reported in previous work [28, 29]. Alteration in morphology is discernable when compared to that of Fe₃O₄ and Fe₃O₄@dopa. Transmission electron microscopy (TEM) images of Fe₃O₄@dopa@MnL¹Cl are depicted in Figure 3. These images reveal that the magnetic nanoparticles are rod-like structures with average diameter of 50 nm. Energy-dispersive X-ray spectroscopy (EDX) spectrum of Fe₃O₄@dopa@MnLCl is depicted in Figure S7. Signals of Fe and O can be attributed to Fe₃O₄ nanoparticles and C from Dopamine. Signals of Mn and Cl can be cited to the complex moiety thus confirming successful surface modification. Results of the magnetic behavior of the Fe₃O₄, Fe₃O₄@dopa and Fe₃O₄@dopa@MnLCl nanoparticles under the applied magnetic field are represented in Figure 4. Values of the saturation magnetization (M_s) diminished from Fe₃O₄ nanoparticles



Figure 4. Magnetic curves of (a) Fe₃O₄, (b) Fe₃O₄@dopa and (c) Fe₃O₄@dopa@MnLCl.

(57.04 emu g⁻¹) to Fe₃O₄@dopa (38.9 emu g⁻¹) and to the final Fe₃O₄@dopa@MnLCl nanocatalyst (25.58 emu g⁻¹) can be accredited to gradual increment of diamagnetic organic materials from Fe₃O₄ to Fe₃O₄@dopa@MnLCl.

3.4. Tuning of catalytic conditions

3.4.1. Epoxidation reaction

In a single reaction, (E)-stilbene (3 mmol) (as representative), HMN (0.01 mmol) and PhI(Oac), (1.3 mmol) were mixed in 10 mL acetonitrile and stirred for 3 h at room temperature. The progress of the reaction was monitored by TLC followed by usual work up and chromatographic purification; the isolated yields of epoxide are 94% in acetonitrile. From this initial experiment we proceeded further to optimize the catalysis conditions, viz amount of catalyst and terminal oxidant, along with the time required to obtain the maximum epoxide yield. To optimize the amount of catalyst, its concentration is varied between 0.01 and 0.1 mmol per 3 mmol of (E)-stilbene. Epoxide yield increased when the amount of catalyst is increased from 0.01 mmol to 0.1 mmol but the yield remains the same with further increment of catalyst up to 0.2 mmol. The reaction was also studied with varying amounts of PhI(OAc) between 0.5 and 1.3 mmol per 3 mmol of (E)-stilbene. The yield of the epoxide was also studied by varying the time between 2 and 6 h. Epoxide yield attained peak after 3 h of reaction and remained the same even after 6 h. An optimum amount of 0.01 mmol of catalyst, PhI(OAc)₂ (3 mmol) and 4 h reaction time are ideal for achieving the best yield. Table 4 represents the epoxide yields under different conditions using HMN as catalyst. The essential role played by the catalyst is evident from the extremely low (< 2%) yield of epoxide found in a blank reaction carried out in absence of the catalyst.

3.4.2. Alcohol oxidation

For oxidation of alcohols, benzyl alcohol (3 mmol) (as representative), **HMN** (0.01 mmol) and Phl(Oac)₂ (2 mmol) were mixed in 10 mL acetonitrile and stirred for 5 h at room temperature (see Scheme 2). The progress of the reaction was monitored by TLC followed by usual work up and chromatographic purification, with isolated yields of aldehyde 90% in acetonitrile.

Catalyst	Substrate	Conversion ^a (%)	TON ^c	Yield ^b (%)	ee (%) ^{d,*}
	(E)-Stilbene	44	24.2	55	25
HMN	(Z)-Stilbene	90	78.3	85 (<i>cis:trans</i> = 60:40)	28 (trans)
	Styrene	85	76.5	90	32
	(E)-Stilbene	92	87.4	95	26
FDM	(Z)-Stilbene	79	67.94	87 (<i>cis:trans</i> = 65:35)	31 (<i>trans</i>)
	Styrene	70	56	80	27
	(E)-Stilbene	82	73.8	90	23

Table 4. Catalytic epoxidation of alkenes in CH_3CN by $PhI(OAc)_2$ using $MnL(CI)(H_2O)$ (**HMN**) and $Fe_3O_4@$ dopa@MnLCI (**FDM**) as the catalysts.

Notes: Reaction conditions: complex (0.01 mmol), alkene (3 mmol), PhI(OAc)₂ (3 mmol), CH₃CN (10 mL) stirred at room temperature for 4 h.

^aDetermined by ¹H NMR analysis of the crude reaction mixture using as internal standard.

^bYields of the respective epoxide are based on 100% conversion of the (E)-stilbene.

^cTurnover number (TON) = [(total number of moles of product)/(moles of catalyst)].

^dDetermined by ¹H NMR (300 Hz) in the presence of Eu(hfc).

*Configuration not determined.

Catalyst	Substrate	Conversion ^a (%)	TON ^c	Yield ^b (%)
	Benzyl alcohol	44	24.2	55
HMN	Benzyl alcohol	95	93.1	98
	1-Octanol	91	83.72	92
	1-Phenylethanol	85	80.75	95
FDM	Benzyl alcohol	90	85.5	95
	1-Octanol	85	73.95	87
	1-Phenylethanol	82	72.16	88

Table 5. Catalytic oxidation of alcohols in CH₃CN by PhI(OAc)₂ using HMN and FDM as the catalysts.

Notes: Reaction conditions: complex (0.01 mmol), alcohol (3 mmol), PhI(OAc)₂ (2 mmol), CH₃CN (10 mL) were stirred at room temperature for 4 h.

^aDetermined by ¹H NMR analysis of the crude reaction mixture using as internal standard.

^bYields of the respective carbonyl products are based on 100% conversion of the benzyl alcohol.

'Turnover number (TON) = [(total number of moles of product)/(moles of catalyst)].

Similar to the procedure followed for epoxidation, here also we attempted to optimize the catalysis conditions, *viz* amount of catalyst and terminal oxidant, along with the time required to obtain the maximum aldehyde yield. To optimize the amount of catalyst, its concentration is varied between 0.01 and 0.2 mmol per 3 mmol of benzyl alcohol. Yield of aldehyde increased when the amount of catalyst is increased from 0.05 mmol to 0.1 mmol but the yield remains the same with further increment of catalyst up to 0.2 mmol. Similarly the reaction has been studied with varying amounts of PhI(OAc)₂ between 1 and 3 mmol per 3 mmol of benzyl alcohol. The yield of the aldehyde was also studied by varying the time between 2 and 6 h. Aldehyde yield attained peak after 5 h of reaction and remained the same even after 6 h. An optimum amount of 0.01 mmol of catalyst, PhI(OAc)₂ (2 mmol) and 5 h reaction time are ideal for achieving the best yield. Table 5 represents the benzyl alcohol oxidation yields under different conditions using **HMN** as catalyst. The essential role played by the catalyst is evident from the extremely low (< 2%) yield of epoxide found in a blank reaction carried out in absence of the catalyst.

3.4.3. Alkane oxidation

For alkane oxidation we selected diphenylmethane as representative. Initially we proceeded by taking diphenylmethane (2 mmol) HMN (0.01 mmol), PhI(Oac)₂ (1.8 mmol) in 10 mL

Catalyst	Substrate	Conversion ^a (%)	TON ^c	Yield ^b (%)
	Diphenylmethane	44	24.2	55
HMN	Ethylbenzene	90	84.6	94
	Diphenylmethane	88	79.2	90
	Tetralene	92	87.4	55 94 90 95 88 86 82
FDM	Ethylbenzene	90	79.2	88
	Diphenylmethane	85	73.10	86
	Tetralene	78	63.96	82

Table 6. Catalytic oxidation of alkanes in CH ₂ CN by I	PhI(OAc), using HMN and FDM as the cataly	sts
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Notes: Reaction conditions: complex (0.01 mmol), alkane (2 mmol), PhI(OAc)₂ (1.8 mmol), CH₃CN (10 mL) were stirred at room temperature for 4 h.

^aDetermined by ¹H NMR analysis of the crude reaction mixture using as internal standard.

^bYields of the respective carbonyl products are based on 100% conversion of diphenylmethane.

^cTurnover number (TON) = [(total number of moles of product)/(moles of catalyst)].

acetonitrile and the mixture was stirred for 6 h at room temperature. To optimize the amount of catalyst, its concentration is varied between 0.01 and 0.2 mmol per 3 mmol of diphenylmethane. Yield of our desired product *i.e.* ketone increased when the amount of catalyst is increased from 0.05 mmol to 0.1 mmol. Similar to alcohol oxidation and epoxidation, here as well the reaction has been studied with varying amounts of PhI(OAc)₂ between 1 and 3 mmol per 2 mmol of diphenylmethane. The yield of the ketone was also studied by varying the time between 2 and 6 h. Yield of our desired product maximized after 6 h of reaction and remained the same even after 10 h. An optimum amount of 0.01 mmol of catalyst, PhI(OAc)₂ (1.8 mmol) and 6 h reaction time were ideal for achieving the best yield of ketone. Table 6 represents the diphenylmethane oxidation yields under different conditions using **HMN** as catalyst. The essential role played by the catalyst is evident from the extremely low (< 2%) yield of epoxide found in a blank reaction carried out in absence of the catalyst.

3.5. Oxidation property of Fe₃O₄@dopa@MnLCl

3.5.1. Epoxidation of alkenes

We determined optimum conditions to achieve maximum epoxide yield as previously done for the homogeneous system. We proceeded by varying the weight of Fe_3O_4 @dopa@MnLCl between 50 and 85 mg per 3 mmol of (*E*)-stilbene. Yield of epoxide heightened when the amount of catalyst is increased from 50 to 90 mg but the yield remained the same with further increment of catalyst to 150 mg. The reaction has also been studied with varying amounts of terminal oxidant, $Phl(OAc)_2$ and time. The results show that using 3 mmol $Phl(OAc)_2$ and 6 h stirring the best epoxidation yield is obtained. At the end of the reaction, the catalyst was magnetically separated and reused for further epoxidation. We did not find any leaching of catalysts during the epoxidation. We studied Fe_3O_4 @dopa@MnLCl catalyzed epoxidation of three different alkenes [(*E*)-stilbene, (*Z*)-stilbene, or styrene] in CH₃CN with Phl(OAc)₂ and the results are presented in Table 4.

3.5.2. Alcohol oxidation

For alcohol oxidation we followed similar optimization process with homogeneous catalysts. We varied the weight of Fe_3O_4 @dopa@MnLCl between 50 and 95 mg per 3 mmol of benzyl alcohol. Yield of aldehyde increased when the amount of catalyst is increased from 50 to 100 mg but the yield remained the same with further increment of catalyst to 150 mg. The

reaction was studied with varying the amounts of $Phl(Oac)_2$ and time. The results show that using 3 mmol $Phl(OAc)_2$ and 6 h stirring, the best epoxidation yield is obtained. At the end of the reaction, the catalyst was magnetically separated and reused for further oxidations. The TEM image and IR spectrum of the reused catalyst are shown in Figures 5 and 6. We did not find leaching of catalyst during the oxidation reaction.

3.5.3. Alkane oxidation

We followed similar optimization process as with homogeneous catalysts, varying the weight of Fe₃O₄@dopa@MnLCl between 50 and 90 mg per 3 mmol of diphenylmethane. Yield of ketone increased when the amount of catalyst is increased from 50 to 100 mg but the yield



Figure 5. TEM image of reused Fe₃O₄@dopa@MnLCl.



Figure 6. FTIR spectra of reused Fe₃O₄@dopa@MnLCl (up to five times).

remained the same with further increment of catalyst to 150 mg. The reaction was studied with varying amounts of $Phl(OAc)_2$ and time. The results show that using 1.3 mmol $Phl(OAc)_2$ and 6 h stirring gave the best epoxidation yield. At the end of the reaction, the catalyst was magnetically separated and reused for further oxidation. We did not find leaching of catalyst during the oxidation reaction.

4. Conclusion

We have synthesized and characterized a new magnetically separable nanocatalyst, $Fe_3O_4@$ dopa@MnLCl. Its capacity to oxidize various organic functionalities was tested with Phl(OAc)₂ as an oxidizing agent and our synthesized nanocatalyst appears to be an efficient catalyst. Comparing our results on alkene epoxidation, alcohol oxidation and alkane oxidation with those of other similar studies [28, 29, 42–44] it can be concluded that the catalyst reported in this work is superior to similar catalysts in terms of reaction conditions, conversion, and yield. Main advantage of our present catalyst is its ease of synthesis and ease of separation. Also the major advantage in this present work is the choice of Phl(OAc)₂ which is superior to any other oxidizing agents such as H_2O_2 , PhIO, *etc.* The method is simple and practical. Gentle reaction conditions, good yields, absence of tedious separation procedures, clean reaction profiles, energy efficiency, as well as the use of inexpensive and environmentally benign catalysts are the key advantages of the present method.

Supplementary material

Figures of infrared spectra, PXRD, TG analysis, SEM and EDX are presented in the Supplementary Material. CCDC 1549539.

Disclosure statement

No potential conflict of interest was reported by the authors.

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