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Layered zinc and lanthanum hydroxide nitrates hosting chiral

sulphonato-(salen)manganese(III) complex catalyzed asymmetric

epoxidation reactions

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Abstract

Layered zinc and lanthanum hydroxide nitrates were first applied as two ion-exchangeable supports for immobilizing a chiral sulphonato-(salen)manganese(III) complex, and the resulted catalysts were characterized by FT-IR, elemental analysis, ICP-AES, TGA, conductivity, XRD, nitrogen physisorption, along with aqueous particle size and zeta potential. Heterogeneous catalysts showed moderate to good conversions and excellent enantioselectivities in epoxidation of styrene and α -methylstyrene when iodosylbenzene was employed as terminal oxidant. Furthermore, the superiority came from heterogeneity, and only filtration could lead to an effective separation of catalyst from product solution.

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Keywords: Layered single-metal hydroxide salt; Sulphonato-(salen)Mn(III); Asymmetric epoxidation; Conversion; Enantioselectivity; Heterogeneity.

1. Introduction

Synthesis and application of enantiomerically pure epoxides are of continuous significance in both synthetic chemistry and pharmaceutical industry [1]. In order for synthetic feasibility, enantiomeric purity, and atom economy as well, the design of effective catalysts for asymmetric epoxidation of alkenes had constituted an important strategy for large-scale production of fine chemicals. Chiral (salen)manganese(III) complexes (salen, N,N'-bis(salicylidene)ethylenediaminato), initially developed by Jacobsen [2] and Katsuki [3], were synthetically accessible, inexpensive and nontoxic, and could afford high enantiomeric excess (e.e.) values as well as conversions in homogeneous catalysis, but exhibited poor catalyst recovery and recycling. Therefore, studies on immobilization had been carried out for purpose of heterogeneous catalysis, such as grafting onto polymers [4], inorganic porous materials [5], and ionic liquids [6]. However, heterogeneous approaches toward ultimate goal were not completely successful up to date. Limited accessibility of substrate to metal centers restricted conversion and enantioselectivity, and catalyst leaching would degrade reactivity and contaminate product [7]. Therefore, exploring porous and stable supporting materials had constituted a real challenge in the future.

Layered double hydroxide (LDH) had attracted attentions due to their potential applications in industry [8]. The layers in LDH were held together through electrostatic or van der Waals forces, and interlayer spaces could be utilized by exfoliation or intercalation. LDH, having a generic formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$ with stable porous structure, had been employed as

catalyst or supporting material into various catalytic reactions [8]. In particular, Anderson [9] and Choudary [10] intercalated a sulphonato-Mn(salen) complex into Zn(II) or Mg(II) / Al(III) LDH to produce active epoxidation catalysts, revealing synergetic effects of salen complex with local environments.

In addition to LDH, another interesting layered material denoted as layered single-metal hydroxide salt (abbreviated as LHS) came into sight, and current studies mainly focused on their synthesis and characterization [11]. When selecting carriers for immobilization of (salen)Mn(III), LHS showed several advantages over LDH. First, synthesis of LHS was easier, and sometimes caused a more regular inner structure than LDH [11]. Next, trivalent cations were scarce in LHS, so interlayer forces were weaker and intercalation of bulkier anions became convenient [11]. At last, LHS offered an opportunity to study novel lanthanide hydroxide layers that might bear some other specific physicochemical properties [12].

In this study, layered zinc and lanthanum hydroxide nitrates were prepared for immobilizing a sulphonato-(salen)Mn(III), and physicochemical characterizations might give structural information. Terminal oxidants including sodium hypochloride (NaClO) and iodosylbenzene (PhIO) were loaded into epoxidations of terminal, *trans*- and cyclic unfunctionalized alkenes, to comprehensively evaluate heterogeneous catalysts.

2. Experimental

2.1. Starting Materials and Syntheses

 $Zn(NO_3)_2 \cdot 6H_2O$, La(OH)₃·6H₂O, styrene, α -methylstyrene, *trans*-stilbene, indene, and HPLC-grade solvents were purchased from Sigma-Aldrich without purification.

 $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (**Zn-LHS**) [13], La(OH)₂(NO₃)·H₂O (**La-LHS**) [13], synthetic intermediates and sulphonato-(salen)Mn(III) (catalyst 1) [14], PhIO [15] were prepared according to literatures. Catalyst 1 (2 mmol) was water-soluble, its ion-exchanging reactions with **Zn-LHS** (2 mmol) or **La-LHS** (4 mmol) were carried out in distilled water (20 mL) with stirring at room temperature, supposing complete ion-exchanging of nitrates with catalyst anions (Fig. 1). Precipitates (both catalysts 2 and 3) were collected by filtration and washed by distilled water (3 × 30 mL), ethanol (3 × 30 mL), and dichloromethane (3 × 30 mL), to remove possibly physisorbed catalyst 1, NaNO₃ or organic impurities.

2.2. Instrumental Conditions

H¹ NMR spectra were acquired on Bruker ADVANCE III (400MHz): CDCl₃ (TMS) for conversions, sample/(CDCl₃ and TMS) 10% (v/v), CDCl₃/TMS 25/1 (v/v), 295.5 K, on integration of methyl hydrogen for α-methylstyrene, and of C=C hydrogen for other olefins, ± 5% relative error of stated values. FT-IR were collected in KBr pellets on Bruker Tensor 27. The C, H, N elemental analyses were carried out on Elementar VarioEL III. Metal contents were obtained through inductive coupled high frequency plasma atomic emission spectrometry (ICP-AES), ICPE-9000. Conductivities were measured on DDS-11A digital conductivity meter in DMSO at 298 K. Thermogravimetric analysis (TGA) was performed on NETZSCH TG 209C with TASC 414/4 controller: 10 K/min, 296 K to 893 K. The BET surface area, pore volume, pore radius, and pore size distribution were recorded on Micromeritics ASAP 2020 at 77.35 K, each sample was degassed in vacuum at 150 °C. Bulk density was recorded on SOTAX TD2 density detector, CAMAG. Aqueous particle size and zeta potential were measured at 298 K on Zetasizer Nano ZS90 spectrometer, Malvern. X-ray diffraction (XRD) were recorded on Shimadzu XRD-6000

X-ray diffractometer (Cu-Ka₁, λ 1.54059 Å), 2 θ angles of 4°-40° at 0.02° intervals. Thin layer chromatography (TLC) was conducted on GF₂₅₄ silica gel, coloration by phosphomolybdic acid (PMA) / ethanol (5% mass percent). HPLC analysis was performed on Waters instrument (system controller: Waters 1525, binary hplc pump; UV-vis detector: Waters 2998, photodiode array detector; UV detection: 242 nm), equipped with a CHIRALCEL OD-H column (150 mm × 4.6 mm; 5 µm particle; mobile phase: *n*-hexane/2-propanol, 93/7, v/v; flow rate: 1.0 mL min⁻¹; column temperature: 300 K; pressure: 4 MPa; sample concentration: 1.0 mg mL⁻¹ in *n*-hexane; injection: 10 µL).

2.3. Catalysis

For NaClO facilitated reactions: Na₂HPO₄ (0.05 mol/L, 4 mL) was added to a commercial NaClO solution (0.58 mol/L, 10 mL) under stirring, buffered pH was 13.1, then pre-cooled at 0°C. Alkene (2 mmol), catalyst (0.12 mmol Mn, 6 mol% on alkene), and NH₄OAc (co-catalyst, 0.24 mmol) were combined with CH₂Cl₂ (5 mL) into a round-bottomed flask (250 mL) with addition funnel at ice-water bath (0 °C). Under vigorous stirring, the pre-cooled NaClO solution was introduced dropwise, and reaction progress was monitored by TLC together with PMA coloration (petroleum ether/CH₂Cl₂, 2/1, v/v; R_f of styrene, α -methylstyrene, *trans*-stilbene, and indene: 0.89, 0.86, 0.72, 0.75; R_f of epoxides for above alkenes: 0.26, 0.23, 0.36, and 0.32 correspondingly). After 6 h, the mixture was diluted with CH₂Cl₂ (30 mL), organic layer was isolated, and heterogeneous catalyst was recovered by filtration under reduced pressure from aqueous suspension. CH₂Cl₂ layer was washed with water (50 mL), brine (50 mL), dried over anhydrous Na₂SO₄. After evaporation, the residue was suitable for ¹H NMR and HPLC. As a reference, the mixture was filtrated after reaction of 6h, and filtrate was monitored by TLC for another 6 h. No

increased conversions were detected by ¹H NMR.

For PhIO facilitated: alkene (2 mmol), catalyst (0.12 mmol Mn, 6 mol% on alkene), iodosylbenzene (2.3 mmol) and NH₄OAc (co-catalyst, 0.24 mmol) were combined with CH₂Cl₂ (5 mL) into a round-bottomed flask (250 mL) at 0 °C. The suspension was stirred vigorously, and monitored by identical TLC. After 6 h, the mixture was diluted with CH₂Cl₂ (30 mL), and solid catalysts were recovered by filtration. CH₂Cl₂ layer was washed with water (50 mL), brine (50 mL), dried over Na₂SO₄. After evaporation, residue was suitable for ¹H NMR and HPLC. Similar reference experiments had proved no further reaction occur after catalyst separation.

3. Results and Discussion

3.1. Characterization of Catalysts

According to Fig. 2, the broad bands at 3500 to 3200 cm⁻¹ for all samples could be ascribed to stretching vibration of water hydroxyls. Remarkably, 3635 and 3574 cm⁻¹ for **Zn-LHS** (**b**), 3583 and 3539 cm⁻¹ for **La-LHS** (**d**) illustrated ZnO-H and LaO-H vibrations [11,13]. Although ZnO-H absorptions were overlapped with water hydroxyls on catalyst **2** (**c**), LaO-H vibrations were still distinctive at the same positions (**e**). Spectra **b**, **d**, **e** showed sharp peaks at 1636, 1645, and 1645 cm⁻¹, which were H₂O bending vibration (arrow labeled) [13]. Absorption at 1608 cm⁻¹ for catalyst **1** was characteristic of C=N stretching that also retained in catalysts **2** and **3** (solid triangles in **a**, **c**, **e**), indicating effective linkage of salen complex with LHSs. Moreover, IR bands at 1191 and 1066 cm⁻¹ stemmed from anti-symmetric and symmetric stretching of SO₃⁻ on catalyst **1** [16], and they were still in catalyst **2** (hollow triangles in **a** and **c**), which further supported grafting. Bands like 1384 cm⁻¹ for **Zn-LHS** and 1384, 1338, 1051 cm⁻¹ for **La-LHS** were all typical vibrations for

nitrates (asterisks in **b** and **d**) [13], but they all shifted or declined after ion-exchanging (asterisks in **c** and **e**), indicating partial replacement of nitrates by anions of catalyst **1**.

C, H, N and metal contents (Table 1), as well as TGA (Fig. S1 in Supplementary data) put forward ideal composition of synthetic products. Zn-LHS and La-LHS contained no carbon, so formula weights of catalysts 2 and 3 could be determined according to carbon with one (salen)Mn(III) as criteria. Referencing the reported thermal behaviors of sulphonato-(salen)Mn(III) [16], Zn-LHS [13], and La-LHS [13], all weight loss below 200 °C could be assigned to water release. Ideal chemical formulae were deduced: $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (**Zn-LHS**), La(OH)₂(NO₃)·H₂O (La-LHS), $C_{28}H_{36}N_2O_8S_2Na_2MnCl\cdot H_2O$ (catalyst 1), C₂₈H₃₆N₂O₈S₂MnCl·[Zn₅(OH)₈]₈(NO₃)₁₄·56H₂O 2), (catalyst and $C_{28}H_{36}N_2O_8S_2MnCl \cdot [La(OH)_2]_{12.5}(NO_3)_{10.5} \cdot 16H_2O$ (catalyst **3**). Featuring (salen)Mn(III) as criteria, both catalysts 2 and 3 showed declined molar conductivities than catalyst 1, and with $[Zn_5(OH)_8]^{2+}$ or $[La(OH)_2]^+$ as standard, catalysts 2 and 3 also exhibited lower conductivities than Zn-LHS and La-LHS, which both proved immobilization of (salen)Mn(III) anions into LHSs through ion-exchanging [17].

The observed interlayer spacing of 9.63 Å (2θ at 9.18°) for **Zn-LHS** was amplified to 12.95 Å (2θ at 6.82°) for catalyst **2** (Fig. 3), but calculated dimension of a solvated Jacobsen's complex was 2.05 nm × 1.61 nm [18], so **Zn-LHS** probably underwent exfoliation and restacking during ion-exchanging [11], and planar catalyst **1** seemed to intercalate with **Zn-LHS** horizontally. Both **Zn-LHS** and catalyst **2** showed approximate type III isotherms with H1 hysteresis loop at higher relative pressure (Fig. 4), revealing a structure composed of uniform spheres in regular array and narrow distributions of pore size [19]. Catalyst **2** showed improved surface area and pore volume

than **Zn-LHS** (Table 2), mainly owing to intercalation. On the other hand, *d*-spacing of 9.64 Å (2θ at 9.16°) for **La-LHS** was slightly shifted to 9.66 Å (2θ at 9.14°) for catalyst **3** (Fig. 3), **La-LHS** and catalyst **3** showed type II isotherms demonstrating monolayer-multilayer adsorption [19], together with an improved surface area of catalyst **3** more than **La-LHS** (Table 2), which all suggested multilayer deposition of (salen)Mn(III) onto **La-LHS** surface instead of intercalation.

3.2. Catalytic Reactions

Blank experiments using Zn-LHS or La-LHS (6 mol% metal on alkene) as catalyst, loading NaClO and PhIO as terminal oxidants for epoxidation of styrene, α -methylstyrene, *trans*-stilbene, and indene had been tested before regular catalyses were summarized in Table 3. Under TLC monitoring during 24 h, neither Zn-LHS nor La-LHS afforded epoxidation product for each substrate. Catalyst 1 could not promote epoxidation reactions with NaClO. The solutions became attenuated and no considerable epoxides were detected on HPLC after 24 h. Perhaps, catalyst 1 was immiscible with CH₂Cl₂ and not in line with phase-transfer condition of ClO⁻ in Jacobsen system [21]. LHS supported (salen)Mn(III) (catalysts 2 and 3), in combination with NaClO, exhibited better conversions for styrene and α -methylstyrene (entries 2, 7, 9). Nevertheless, NaClO was aqueous and water molecules were easily coordinated to Zn(II) and La(III) centers, once channels were occupied by water, the entrance of bulkier olefins to (salen)Mn(III) was mainly blocked that affected conversions (entries 12, 14, 17, 19). When PhIO loaded as oxidant, catalysts 1 to 3 afforded pronounced conversions more than those performed under NaClO, especially for trans-stilbene (entries 11, 13, 15). Furthermore, catalyst 2 consistently afforded higher conversions for all substrates than catalyst 3 (entries 3 vs. 5, 8 vs. 10, 13 vs. 15, 18 vs. 20), probably owing to sandwiched structure of catalyst 2 (Fig. 1 and Fig. 3).

Under PhIO, catalyst 1 exhibited good to moderate enantioselectivity for styrene (entry 1), indene (entry 16), and α -methylstyrene (entry 6), but catalysts 2 and 3 showed great e.e. values for styrene (entries 3, 5) and α -methylstyrene (entries 8, 10). Catalyst 2 provided best recycling for styrene and α -methylstyrene (entries 3, 8). Enantioselective epoxidation of styrene and α -methylstyrene was difficult not only because these terminal alkenes may undergo addition by (salen)Mn(III) with lower enantiofacial selectivity than *cis*-disubstituted and trisubstituted alkenes, but for a nonstereospecific cyclization leading to enantioselectivity leakage [22]. However, this dilemma could be ameliorated by immobilizing (salen)Mn(III) onto appropriate carriers whose spatial effects might do work [23]. Catalyst 2 had an sandwich-type local structure featuring interlayer spacing of 12.95 Å which was narrower than that found in LDH-supported (salen)Mn(III) [9], probably constraining free rotation of styrene or α -methylstyrene in favor of enantioselectivity. Acceptable e.e. values were observed for indene with catalysts 2 and 3, but they were less significant due to low conversions (entries 18 and 20). Additionally, trans-stilbene was not an appropriate substrate, only catalyst 2 afforded a 48 % e.e. together with 50 % conversion (entry 13).

4. Conclusion

In summary, LHS-supported catalysts had specific local structures and exhibited moderate to good conversions, excellent enantioselectivities, as well as satisfactory recycling in epoxidation of styrene and α -methylstyrene under iodosylbenzene as terminal oxidant. Another superiority of this system appeared to be heterogeneity. Herein, only filtration could lead to effective separation of catalyst from product solution.

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Figure Captions

Fig. 1. Synthesis of catalysts. Conditions: i) K_2CO_3 , ethanol/water, 70 °C, 2 h; ii) $Mn(OAc)_2 \cdot 4H_2O$, ethanol/water, N_2 protection, 75 °C, 2 h; NaCl, open system, 1 h; iii) $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$

(Zn-LHS)/Cat. 1, 1/1 (molar ratio); distilled water, 72 h; iv) La(OH)₂(NO₃)·H₂O (La-LHS)/Cat.

1, 2/1 (molar ratio); distilled water, 72 h.

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Fig. 2. FT-IR spectra of catalyst 1 (a), Zn-LHS (b), catalyst 2 (c), La-LHS (d), catalyst 3 (e).

Fig. 3. Powdered XRD patterns of Zn-LHS, catalyst 2, La-LHS and catalyst 3.

Fig. 4. N₂ adsorption-desorption isotherms and pore size distributions of Zn-LHS, La-LHS,

catalysts 2 and 3.



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Fig. 4. N₂ adsorption-desorption isotherms and pore size distributions of Zn-LHS, La-LHS, catalysts 2 and 3.

Table 1

Sample	Elemental analysis ^b			Mn ^c	Zn ^c	La ^c	C/Mn ^d	$\Lambda^{\rm e}$
	С	Н	N					
Zn-LHS	-	1.9 (1.9)	4.4 (4.5)	-	8.10 (8.05)	K	-	190
La-LHS	-	1.6 (1.5)	5.3 (5.5)	-	- Q-	3.99 (3.95)	-	35
Cat. 1	45.9 (45.0)	5.9 (5.1)	4.4 (3.8)	1.39 (1.34)	- ()	-	27.0	187
Cat. 2	5.4 (5.4)	3.0 (3.4)	3.2 (3.6)	0.16 (0.16)	6.39 (6.40)	-	28.1	19
Cat. 3	8.9 (8.9)	2.7 (2.4)	4.0 (4.6)	0.27 (0.26)		3.37 (3.30)	27.4	20

Chemical composition of supporting materials and catalysts^a.

^a Data in parentheses were calculated values based on ideal formulae.

^b Weight percentage (wt%).

^c Determined by ICP (mmol g⁻¹).

^d Molar ratio of Carbon to Mn.

^e Conductivity (ohm⁻¹ cm⁻¹) detected in DMSO: $[Mn^{3+}] 1.0 \times 10^{-3} \text{ mol } L^{-1}$ for catalysts **1** to **3**, $[Zn_5(OH)_8]^{2+} 8.0 \times 10^{-3}$

mol L^{-1} for **Zn-LHS** and catalyst **2**, $[La(OH)_2]^+ 12.5 \times 10^{-3}$ mol L^{-1} for **La-LHS** and catalyst **3**.

Table 2

Sample	$S_{\rm BET}{}^{\rm a}$	PV^b	PR ^c	$ ho^{ m d}$	$d_{\rm S}^{\rm e}$	$d_{\mathrm{W}}{}^{\mathrm{f}}$	Ç
Zn-LHS	3.78	3.07×10^{-2}	134.92	1.56	1.01×10^3	483.5	-29.0
Cat. 2	21.79	$9.38\times10^{\text{-}2}$	73.77	1.07	257	500.2	-28.0
La-LHS	0.63	$1.90 imes 10^{-3}$	52.72	2.91	3.27×10^3	536.9	-30.4
Cat. 3	62.14	$7.31\times10^{\text{-2}}$	30.25	1.70	56.79	596.3	-29.1

Physicochemical properties of supporting materials and catalysts.

^a Surface area determined by BET method based on nitrogen adsorption (m² g^{-1}).

^b Pore volume, BJH method on adsorption (cm³ g⁻¹).

^c Pore radius, BJH method on adsorption (nm).

^d Bulk density (g cm⁻³).

^e Crystallite size based on BET surface area: $d_{\rm S} = 6/(S_{\rm BET} \rho)$, ρ bulk density, nm as unit.

^f Diameter of aqueous particle (nm).

^g Zeta potential of aqueous particle (mV).

Table 3

Entry	Alkene	Catalyst	Oxidant	Conversion ^a (%)	E.e. ^d (%)	$TOF^{e}(h^{-1})$
1		1	PhIO	55	82	1.5
2		2	NaClO	60	23	1.7
3		2	PhIO	39 (40, 40, 36) ^b	99 (99, 99, 94)	1.1
4		3	NaClO	25	78	0.7
5		3	PhIO	37 (35, 30, 27)	99 (99, 85, 80)	1.0
6		1	PhIO	29	55	0.8
7		2	NaClO	52	68	1.4
8		2	PhIO	79 (77, 77, 70)	99 (99, 97, 97)	2.2
9		3	NaClO	49	72	1.4
10		3	PhIO	47 (45, 40, 29)	99 (90, 86, 81)	1.3
11	H Ph	1	PhIO	46	17	1.3
12	Ph H	2	NaClO	NF ^c	-	-
13		2	PhIO	50	48	1.4
14		3	NaClO	NF	-	-
15		3	PhIO	19	20	0.5
16		1	PhIO	33	65	0.9
17		2	NaClO	9	23	0.3
18		2	PhIO	5	56	0.1
19		3	NaClO	4	6	0.1
20		3	PhIO	4	89	0.1

Enantioselective epoxidation of unfunctionalized alkenes catalyzed by catalysts 1, 2, and 3.

^a Determined by ¹H NMR.

^b Values in parentheses were consecutively recycled results.

^c NF: no epoxides were found on HPLC.

^d Determined by chiral HPLC. Major epoxide enantiomers: (*R*)-styrene oxide [20], (*R*)- α -methylstyrene oxide [20],

(1R,2R)-trans-stilbene oxide [20], (1R,2S)-indene oxide [21], after comparison with literatures.

 e Turnover frequency of fresh catalysis, $mol_{product}$ $mol_{Mn}{}^{-1}$ (6 h) $^{-1}.$

Graphical abstract

Layered Zinc Hydroxide Nitrate Hosted Chiral (salen)Mn(III) for Epoxidation



E. e. (%) 99 99 99 94 Conv. (%) 39 40 40 36 E. e. (%) 99 99 97 97 Conv. (%) 79 77 77 70

Highlights

- 1. Chiral (salen)Mn(III) was immobilized into layered hydroxide salts.
- 2. Heterogeneous catalysts showed excellent e.e. values for terminal alkenes.
- 3. Recycling experiment of heterogeneous catalysts was satisfactory.
- 4. Superiority of this system appeared to be heterogeneity.

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