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# Non-redox metal ions accelerated oxygen atom transfer by $Mn-Me_3$ tacn complex with $H_2O_2$ as oxygen resource



# Zhanao Lv, Cholho Choe, Yunfeng Wu, Haibin Wang, Zhuqi Chen\*, Guangxing Li, Guochuan Yin\*

Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education; Hubei Key laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

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# ABSTRACT

This work demonstrates a novel strategy that the introduction of non-redox metal ions as Lewis acids to the classic dinuclear manganese complex  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  can greatly promote the alkene epoxidation efficiency under mild conditions with  $H_2O_2$  as the solely terminal oxidant because of its economic and environmental advantages. When  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  was used as the catalyst in the absence of Lewis acids, only 16.4% conversion of cyclooctene with 6.2% yield of epoxide was obtained and the obvious decomposition of  $H_2O_2$  was observed. However, the oxygen transfer efficiency of the catalyst was sharply improved with 100% conversion and 90.2% yield of epoxide under identical conditions when the non-redox metal ion, such as  $Sc^{3+}$ , was introduced to the catalytic system. The novel strategy was successfully applied to the epoxidation reactions of different types of alkenes. Through UV–vis, FT-IR, EPR and CV characterizations, it was evidenced that the non-redox metal ions with high positive charge as Lewis acids could dissociate the sluggish dinuclear  $Mn_{-}(\mu-O)_{-}Mn^{IV} = O$  or  $O = Mn^{IV}$ -( $\mu$ -O)- $Mn^{IV} = O$ , was proposed as the active species, which was capable of the alkene epoxidation process. This work illustrated an alternative protocol to manipulate the reactivity of those sluggish catalysts by the introduction of non-redox metal ions and provided clues to understand the role of non-redox metal ions in metalloenzymes and heterogeneous catalysts.

## Introduction

Manganese complexes have attracted considerable attentions because of its significant roles in a series of biological metabolisms and chemical oxidation processes, such as the oxygen evolution complex (OEC) of photosystem II (PSII) in water oxidation and the synthetic Mn catalysts in the oxo functionalization of hydrocarbons. The synthetic dinuclear manganese(IV) complex  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  (as shown in Scheme 1, Me3tacn is 1,4,7-trimethyl-1,4,7-triazacyclononane) [1], and its derivatives have been revealed to be efficacious catalysts for the oxidation of a broad range of organic functional groups in the presence of carboxylic acids as additives, using both homogeneous [2-30] and heterogeneous [18,31-35] analogues, including olefin epoxidation [2-15] and dihydroxylation [4-6,16-18], alcohol oxidation [11,19-22], sulfide and sulfoxide oxidation [9,21,23-25], and alkane activation [8,26-28]. Studies on these manganese complexes disclosed that Mn-Me3tacn is a good system for developing model compounds of manganese-containing biologically important enzymes.

It is noteworthy that almost no oxidation reaction can be observed in the absence of carboxylic acid in all cases mentioned above. The carboxylic acids as additives are essential to suppress the unwanted catalase-like decomposition of hydrogen peroxide and achieve high catalyst productivity and selectivity. Although the acids have been proposed to form adducts with the Mn complex, the precise nature of the active intermediate and the role of the carboxylic acids remain unclear.

Alternatively, non-redox metal ions have been realized to play significant roles in various oxidation processes. For instance, it is well known that certain non-redox metal ions are contained in the oxidative reaction of metalloenzymes such as the oxygen evolution of Photosystem II in which  $Ca^{2+}$  is one essential component of the active  $Mn_4O_5Ca$  center [36–41], and many non-redox metal ions are frequently employed as additives in heterogeneous catalysts to modify the reactivity and stability of the redox catalysts [42–46]. Therefore, nonredox metal ions offer another feasible strategy for regulating the reactivity of redox metal ions through its bridge or ligation with the metal oxo functional groups in a number of homogeneous reactions [47–60].

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<sup>\*</sup> Corresponding authors. E-mail addresses: zqchen@hust.edu.cn (Z. Chen), gyin@hust.edu.cn (G. Yin).



Scheme 1. Chemical structure of [Mn<sub>2</sub><sup>IV</sup>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> catalyst.

Addressing the functional roles of non-redox metal ions is highly related to the mechanism of both metalloenzymes in nature and multimetallic catalysts in chemical oxidation, and their roles have attracted considerable attentions in both the biological and chemical communities [36–76].

In our previous works, the effective strategy of introducing non-redox metal ions as Lewis acids was widely applied to modulate the reactivity of transition metal catalysis including manganese, iron, palladium, vanadium, ruthenium and osmium complexes in versatile homogeneous reactions, such as hydroxylation, N-dealkylation, C-C coupling, dehydrogenation, isomerization and epoxidation [61-76]. Recently, we have communicated the first example that the addition of non-redox metal ions can greatly improve the oxygen atom transfer efficiency in catalytic epoxidation by dissociating the dinuclear Mn<sup>III</sup>-(µ-O)<sub>2</sub>-Mn<sup>IV</sup> complex which is very sluggish for olefin epoxidation [74-76]. We further compared the promotion effect of Lewis acid with that of Brønsted acid and found that they showed very similar reaction pathway and promotion effect. However, the organic oxidant, PhI(OAc)<sub>2</sub>, was used in these cases, while all other oxidants including H<sub>2</sub>O<sub>2</sub> were not efficient, giving sluggish performance. For economic and environmental reasons, catalytic olefin oxidations based on H2O2 are preferred over traditional stoichiometric oxidations because of its low cost, high atom efficiency and environmentally benign by-product (water) [77-80].

In the previous reports by other groups, it was found that  $H_2O_2$  was sharply decomposed by the classic dinuclear manganese complex,  $[Mn_2^{V}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , in the acetonitrile solution [10,23,81]. Although the unwanted manganese-catalysed self-destruction of  $H_2O_2$  could be suppressed by the application of acetone as the reaction solvent, this proposal was not acceptable for large-scale synthesis because of the risk of generation of explosive cyclic peroxides. These findings provide a challenge for us to explore whether the wasteful catalase-like decomposition can be suppressed by the introduction of non-redox metal ions serving as Lewis acids with acetonitrile as the solvent.

Encouraged by the classic Mn-Me<sub>3</sub>tacn complexes and the effective strategy of introducing non-redox metal ions, herein, we have investigated the oxygen atom transfer reaction of alkene catalysed by the dinuclear manganese(IV) complex  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  with H<sub>2</sub>O<sub>2</sub> as the solely terminal oxidant in the promotion of non-redox metal ions. Compared with the effect of carboxylic acids in abundant reports, the introduction of non-redox metal ions as Lewis acid can also induce the remarkably promotional effect by dissociating the dinuclear  $Mn-(\mu-O)_3$ -Mn core in the epoxidation reaction and better efficiency is observed in the case of Lewis acids with higher positive charge. The primary mechanism in catalytic process was further explored and the open-loop dinuclear manganese complex was proposed as the key active species to be capable of the alkene epoxidation process. This work demonstrates a novel strategy to improve the catalytic reactivity of some µ-oxo-bridged complexes and inspires us to explore novel catalysts for current challenges and societal demands.

#### **Experimental section**

#### Chemicals

All chemicals were commercially available and used without further purification unless otherwise indicated. The non-redox metal salts, such as

sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate (Mg(OTf)<sub>2</sub>), scandium trifluoromethanesulfonate (Sc(OTf)<sub>3</sub>), ytterbium trifluoromethanesulfonate (Yb(OTf)<sub>3</sub>) and yttrium trifluoromethanesulfonate (Y(OTf)<sub>3</sub>) came from Accela ChemBio Co., Ltd or Alfa Aesar. Other trifluoromethanesulfonates including Ca(OTf)2, Ba (OTf)<sub>2</sub>, Zn(OTf)<sub>2</sub> and Al(OTf)<sub>3</sub> were purchased from Aladdin or Shanghai Dibai Chemical Company. The alkenes, such as cyclooctene, cyclohexene, norbornene, styrene, 1-hexene and 1-dodecene, and their corresponding epoxides were obtained from Aldrich, Alfa Aesar or TCI (Shanghai) Development Co., Ltd. Ammonium hexafluorophosphate was purchased from Alfa Aesar. Common solvents, H<sub>2</sub>O<sub>2</sub> (30% aqueous solution) and inorganic manganese salt, MnCl<sub>2</sub>•4H<sub>2</sub>O, came from Sinopharm Chemical Reagent Co., Ltd. The ligand, 1.4.7-trimethyl-1.4.7-triazacyclononane (Me3tacn), and its corresponding dinuclear manganese(IV) complex,  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , were synthesized according to the previous literature procedures [82-84], and the chemical structure of  $[Mn_2^{IV}(\mu$ - $O_3(Me_3tacn)_2](PF_6)_2$  is displayed in Scheme 1.

#### Characterization equipment

Gas chromatography-mass spectrometry (GC-MS) analysis was conducted on an Agilent 7890A/5975C spectrometer. FT-IR spectra were collected on a Bruker VERTEX70. UV-vis spectra were obtained on an Analytik Jena Specord 205 UV-vis spectrometer. Electron paramagnetic resonance (EPR) experiments were performed at 130 K on a Bruker A200 instrument, with a center field of 3352.488 G, frequency of 9.395 GHz, power of 19.44 mW, modulation amplitude of 2.00 G and receiver gain of  $1.00 \times 10^3$ . The content of Mn ion was determined by atomic absorption spectroscopy (AAS) analysis with an Analyst 300 Perkin Elmer. Mass spectra (MS) were measured in negative mode in the range m/z 50–3000 by a Bruker SolariX 7.0T spectrometer (ESI-MS). Elemental analysis (EA) was performed on a Vario Micro cube. Cyclic voltammetry (CV) were conducted with a CS CorrTest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as the reference electrode. Electrochemical data were collected in dry acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

#### Reaction procedure

#### General procedure for non-redox metal-ions-accelerated alkene epoxidation by the dinuclear manganese(IV) complex

The solution of 5 mL of acetonitrile containing 0.1 M alkene, 1 mM dinuclear manganese(IV) complex and 2 mM non-redox metal salt as Lewis acid was cooled in an ice water bath (273 K). Then 1.5 mmol  $H_2O_2$  (30% aqueous solution) was added to the mixture solution to initialize the reaction. The reaction mixture was magnetically stirred at 273 K in the ice water bath for 2 h (set intervals for kinetics study). The yield of epoxide and the conversion of alkene were quantitatively analyzed by GC using the internal standard method. Control experiments using the dinuclear manganese (IV) complex or different non-redox metal salts alone as the catalyst were performed in parallel under identical conditions. All the reactions were conducted at least in triplicate and the average data were applied in the results and discussion section.

#### **Results and discussion**

#### Non-redox metal-ions-accelerated effect in alkene epoxidation

The promotional effect with non-redox metals on epoxidation was initially conducted with cyclooctene as the typical substrate and  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  as the catalyst, during which  $H_2O_2$  was applied as the solely terminal oxidant. The catalytic epoxidation experiments in the promotion of trivalent metals like  $Al^{3+}$  and  $Sc^{3+}$  were investigated at different reaction temperatures as shown in Table S1.

Although a reaction temperature of 303 K accompanied a faster reaction rate in the initial 30 min, a lower reaction temperature of 273 K was beneficial to the selectivity of epoxide. Meanwhile, when the trivalent metal of Al<sup>3+</sup> was added at 303 K, the observable decomposition of  $H_2O_2$  and the oxygen release were obtained, which led to the incomplete conversion of cyclooctene (82.1% conversion and 55.8% yield). The similar phenomenon was also observed in the addition of 4 equiv. of Sc<sup>3+</sup> and the influence of Sc(OTf)<sub>3</sub> concentration on the catalytic epoxidation was tested and summarized in Table S2 and Fig. S4. As illustrated in Fig. S4, the continuously remarkable promotion was observed with the increasing Sc(OTf)<sub>3</sub>/Mn<sub>2</sub><sup>IV</sup> ratio from 0 to 2, accompanied by the conversion from 16.4% to 100%. However, when the ratio of Sc(OTf)<sub>3</sub>/Mn<sub>2</sub><sup>IV</sup> was further increased to 4, the conversion decreased to 76.5% with a yield of 52.0%. The complementary experiments have clearly disclosed the synergistic effect of Sc(OTf)<sub>3</sub> and revealed that 2 equiv. of non-redox metal ion (relative to the dinuclear manganese catalyst) has already displayed a saturated amount to interact with the dinuclear manganese and then form the active species for epoxidation. The reaction temperature of 273 K and 2 equiv. of Sc (OTf)<sub>3</sub> were selected in following experiments.

The promotional effect by different non-redox metal ions as additives was compared in Table 1. When the dinuclear manganese complex,  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , was used as the catalyst in the absence of non-redox metals, the obvious oxygen release from the decomposition of H2O2 was observed, and only 16.4% of alkene was converted with 6.2% yield of 1,2-epoxycyclooctane (Table 1, entry 1). This result indicated that the dinuclear manganese complex alone was obviously a sluggish catalyst for the alkene epoxidation, which was consistent with previous reports [2-15]. When non-redox metal ions were added to the reaction solution of the dinuclear manganese catalyst, the oxygen release was greatly suppressed by naked eyes and a remarkably synergistic effect in epoxidation was obtained, especially in the case of non-redox metal ions with higher positive charges. For instance, adding 2 equiv. of Ba<sup>2+</sup> improved the conversion of alkene up to 42.8% with 30.7% yield (Table 1, entry 5), while almost 100% conversion was demonstrated in the cases of trivalent metal ions such as Sc<sup>3+</sup> and Al<sup>3+</sup> under identical conditions with 90.2% and 87.0% yield of product, respectively (Table 1, entry 9 and 10). Meanwhile, the control experiments with Lewis acid alone as the catalyst provided less than 5% conversion of cyclooctane in all the cases as displayed in Table S5. Furthermore, it was noteworthy that only 24.5% conversion of cyclooctane and 15.9% yield of epoxide were obtained in the presence of 6 equiv. of NaOTf (Table 1, entry 2), indicating that the promotional effect was not attributed to the influence of extra OTf<sup>-</sup> anions because it contained the identical amount of OTf<sup>-</sup> anions as those in 2 equiv. of trivalent metals. For the purpose of comparison with proton acid used in previous works and excluding the speculation that the promotional

Table 1

Catalytic epoxidation of cyclooctene by  $[Mn_2^{IV}(Me_3tacn)_2(\mu-O)_3](PF_6)_2 H_2O$  with various Lewis acids in the presence of  $H_2O_2$  as oxidant.

Entry	Additives	Conv. (%)	Yield (%)
1	-	16.4 (0.4)	6.2 (0.2)
$2^{a}$	NaOTf	24.5 (0.5)	15.9 (0.3)
3	Mg(OTf) <sub>2</sub>	38.4 (0.8)	26.5 (0.6)
4	Ca(OTf) <sub>2</sub>	39.8 (1.0)	29.3 (0.4)
5	Ba(OTf) <sub>2</sub>	42.8 (0.8)	30.7 (0.6)
6	Zn(OTf) <sub>2</sub>	48.2 (1.0)	33.9 (1.2)
7	Yb(OTf) <sub>3</sub>	83.2 (0.7)	65.8 (0.4)
8	Y(OTf) <sub>3</sub>	89.4 (0.8)	75.5 (0.6)
9	Al(OTf)3	98.7 (0.4)	87.0 (0.8)
10	Sc(OTf) <sub>3</sub>	100 (0.1)	90.2 (1.0)
11 <sup>a</sup>	HOAc	36.8 (1.2)	25.7 (0.8)

Conditions: acetonitrile 5 mL, cyclooctene 0.1 M,  $[Mn_2(Me_3tacn)_2(\mu-O)_3](PF_6)_2\cdot 1$  mM, Lewis acid 2 mM,  $H_2O_2$  0.3 M, 273 K, 2 h; a: additive 6 mM. Data in parentheses represent the deviations.



Fig. 1. Lewis acids-accelerated epoxidation kinetics by  $[Mn_2^{IV}(Me_3tacn)_2(\mu-O)_3](PF_6)_2$  catalyst. Conditions: acetonitrile 5 mL, cyclooctene 0.1 M,  $[Mn_2^{IV}(Me_3tacn)_2(\mu-O)_3](PF_6)_2$  1 mM, Lewis acid 2 mM (6 mM in the case of NaOTf),  $H_2O_2$  0.3 M, 273 K.

effect of non-redox metal ions was originated from the hydrolysis reaction of metal salts with water of  $H_2O_2$  aqueous solution to form proton acid, the epoxidation reaction was performed in the presence of 6 equiv of HOAc (Table 1, entry 11). Although slightly improved performance was observed with 36.8% conversion and 25.7% yield, the reaction activity was not comparable to the cases of trivalent non-redox metals as additives. The above results clearly revealed that the promotional effect was originated from the interaction of non-redox metal ions and the dinuclear manganese complex.

The detailed catalytic kinetics of cyclooctene epoxidation further evidenced the synergistic effect in the addition of different non-redox metal ions (Fig. 1 and Fig. S5). The dinuclear manganese complex alone as the catalyst showed apparently sluggish catalytic process, even in the addition of monovalent metal ion, such as Na<sup>+</sup>. Surprisingly, the addition of non-redox metal ions with higher positive charges such as trivalent metals could remarkably accelerate the epoxidation reaction and displayed a faster reaction rate with a higher yield of epoxide than using manganese catalyst alone. The catalytic kinetics once again revealed that the activity improvement was Lewis acidity strength dependent on the added non-redox metal ions.

We have also extrapolated many major kinetic parameters from the kinetic experiments with different Lewis acids. As displayed in Fig. S22 and Table S6, the initial rate of epoxidation reaction was affected by the nature of the Lewis acid. For example, trivalent metal ions show the highest rate constant ( $0.03945 \text{ min}^{-1}$  in the case of  $\text{Sc}^{3+}$  and  $0.03335 \text{ min}^{-1}$  in the case of  $\text{Al}^{3+}$ ). Meanwhile, non-redox metal ions with a positive charge of 2+ show a relatively low rate constant compared with the trivalent metal ions, such as  $0.00495 \text{ min}^{-1}$  in the presence of  $\text{Zn}^{2+}$  and  $0.00348 \text{ min}^{-1}$  in the addition of  $\text{Mg}^{2+}$ . Adding 6 equiv. of NaOTf only slightly improved the rate constant from  $0.0011 \text{ min}^{-1}$  (for the dinuclear manganese catalyst alone) to  $0.00195 \text{ min}^{-1}$ . Notably, the above rate constant of epoxidation reaction is generally dependent on Lewis acid strength, that is, metal ions with higher positive charge demonstrate better efficiency in promoting olefin epoxidation with the manganese catalyst.

In the epoxidation reaction of other types of alkenes, including cyclic olefins and chain olefins, the synergistic effect between non-redox metal ions and  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  was also observed, and results were summarized in Table 2.  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  or non-redox metal ions alone as the catalyst displayed very sluggish catalytic activity for epoxidation in all the tested substrates. These reactions were greatly promoted in the presence of 2 equiv. of Sc<sup>3+</sup> under the identical conditions. For example, as well as cyclooctene, the cyclic

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Table 2			
Sc(OTf) <sub>3</sub> accelerated	alkene epoxidations l	by [Mn <sub>2</sub> (Me <sub>3</sub> tacn) <sub>2</sub> (μ-C	) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> catalyst.

Entry	alkene	Product	$Mn_2^{IV}$ : Sc <sup>3+</sup>	Conv. (%)	Yield (%)
1 (	$\frown$	$\frown$	0:0	2.0 (0.4)	0.3 (0.2)
	cyclooctene	0 1,2-epoxycyclooctane	0:2	3.8 (1.2)	0.7 (0.4)
	$\searrow$		1:0	16.4 (0.4)	6.2 (0.2)
2			1:2	100 (0.1)	90.2 (1.0)
	$\frown$	$\frown$ is a set	0:0	1.6 (0.3)	0.1 (0.1)
	cyclohexene	Co 1,2-epoxycyclohexane	0:2	3.5 (1.0)	0.7 (0.2)
	~	*	1:0	10.6 (1.8)	3.8 (0.9)
3			1:2	96.4 (1.4)	85.7 (1.2)
	$\frown$		0:0	3.1 (0.5)	0.2 (0.1)
	norbornene	o epoxynorbornylene	0:2	3.5 (0.5)	0.5 (0.2)
	$\checkmark$	$\checkmark$	1:0	16.8 (0.9)	7.7 (1.0)
4 [			1:2	95.3 (1.9)	86.9 (1.8)
			0:0	2.4 (0.6)	0.3 (0.1)
	styrene	epoxystyrene	0:2	4.7 (0.4)	0.3 (0.1)
	*		1:0	9.5 (1.0)	4.6 (0.7)
5 <sup>a</sup> 6 <sup>a</sup>			1:2	92.8 (1.9)	79.4 (1.4)
	1-hexene	$\sim 1.2$ -epoxybexene	0:0	1.3 (0.3)	0.2 (0.1)
			0:2	1.9 (0.6)	0.3 (0.1)
			1:0	7.6 (0.8)	4.0 (0.7)
			1:2	97.2 (1.7)	88.6 (1.4)
	1-dodecene	$\sim$ $\sim$ $\sim$ $\sim$ $\sim$ $1,2$ -epoxydodecene	0:0	1.0 (0.3)	0.3 (0.1)
			0:2	8.6 (1.0)	3.5 (0.3)
			1:0	6.2 (0.7)	2.1 (0.4)
			1:2	99.8 (0.2)	68.7 (1.9)

Conditions: acetonitrile 5 mL, olefin 0.1 M, [Mn<sub>2</sub>(Me<sub>3</sub>tacn)<sub>2</sub>(µ-O)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> 1 mM, Sc(OTf)<sub>3</sub> 2 mM, H<sub>2</sub>O<sub>2</sub> 0.3 M, 273 K, 2 h a:1.5 h. Data in parentheses represent the deviations.

olefin like norbornene could also be converted to epoxide with 95.3% conversion and 86.9% yield within 2 h. Similar promotional effects by the introduction of non-redox metal ions are also obtained in the cases of terminal linear olefins such as 1-hexene and 1-dodecene. One may see that, the conversion of 1-hexene was increased from 7.6% to 97.2% by the addition of  $Sc^{3+}$  to the dinuclear manganese complex, accompanied by the yield of 1,2-epoxyhexene from 4.0% to 88.6%. In particular, the relatively low yield of epoxide in the case of 1-dodecene can be attributed to the over oxidation of 1,2-epoxyhexene. The data in Table 2 clearly disclosed that the accelerated epoxidation strategy by the addition of non-redox metal ions can be workable for various alkene epoxidation reactions.

#### Reaction mechanism

The above data clearly demonstrated that an interaction exists between non-redox metal ions and the dinuclear manganese complex,  $[Mn_2(Me_3tacn)_2(\mu-O)_3](PF_6)_2$ , and the generated active species from them is capable of the alkene epoxidation reaction. As above-mentioned, we have communicated the first example that the addition of non-redox metal ions as Lewis acids can greatly promote the oxygen atom transfer efficiency in catalytic epoxidation by dissociating the two oxygen bridges of the dinuclear  $Mn^{III}$ -( $\mu$ -O)<sub>2</sub>-Mn<sup>IV</sup> complex which is very sluggish for olefin epoxidation [74-76]. In the previous works about the  $[Mn_2^{IV}(Me_3tacn)_2(\mu-O)_3](PF_6)_2/carboxylic acids catalytic$ system reported by other groups, they identified the carboxylic acids as proton source to crack the µ-oxo-bridged Mn-O-Mn species and then as bridging ligand to stabilise the active manganese intermediate [2–15]. Inspired by the previous reports from other groups and us, we have investigated the origins of the promotional effect and the role of nonredox metal ions by stoichiometric experiments, UV-vis, FT-IR, EPR and CV characterizations.

Firstly, for the purpose of checking whether the active intermediate can be generated in situ by the interaction of  $\mathrm{Sc}^{3+}$  and  $[\mathrm{Mn}_2(\mathrm{Me}_3\mathrm{tacn})_2(\mu-\mathrm{O})_3](\mathrm{PF}_6)_2$  in the absence of  $\mathrm{H}_2\mathrm{O}_2$ , the stoichiometric epoxidation reactions were conducted in the presence/absence of oxidant and the results were listed in Table S4. The process of epoxidation reaction almost cannot be proceeded in the absence of  $\mathrm{H}_2\mathrm{O}_2$  with only 3.4% conversion of cyclooctene in 2 h. However, the

stoichiometric epoxidation reaction was rapidly accomplished in the addition of  $H_2O_2$  with 100% conversion within 60 min. The supplementary experiments clearly indicated that the presence of  $H_2O_2$  was necessary to trigger the epoxidation reaction and generate the active species from the interaction of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  and Sc (OTf)<sub>3</sub>.

Then UV-vis characterization was used to detect the interaction of the dinuclear manganese complex and non-redox metal ions. As displayed in Fig. S6, the UV-vis absorption spectrum of [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> is consistent with the previous reports and the characteristic signals from the µ-oxo-bridged Mn-O-Mn at 400 nm and 495 nm are clearly observed [83,85,86]. The absorption band at 400 nm is assigned to the contribution of the Mn<sup>IV</sup> d-d transitions and the band at 495 nm is assigned to ligand to metal charge transfer (LMCT) of oxo ligands to  $Mn^{IV}$  ion [34,83–86]. The UV-vis spectra of [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> or Sc(OTf)<sub>3</sub> are illustrated in Fig. 2a. When H<sub>2</sub>O<sub>2</sub> as oxidant is added to the dinuclear Manganese catalyst, the spectrum of [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> remains unchanged within enough reaction time, and the oxygen release is observed. The control experiment indicated that the dinuclear structure with three oxygen bridges of [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> was maintained, which were verified by the above epoxidation reaction and the previous reports. Adding Sc(OTf)<sub>3</sub> to the solution of dinuclear manganese complex in the absence of H<sub>2</sub>O<sub>2</sub> results in the formation of a new species, accompanying the absorbance band maximum at 316 nm (blue line, Fig. 2a). The new species was assigned to a mononuclear manganese(IV) complex [3] and was generated by the Lewis acid-induced dissociation of Mn-(µ-O)3-Mn core as reported in our previous works [74–76].

In the presence of  $H_2O_2$ , the introduction of Sc(OTf)<sub>3</sub> causes the gradual decay of the absorbance band, including the Mn-O-Mn signals at 400 nm and 495 nm. The decayed process is displayed in Fig. 2b, indicating the formation of a new manganese complex, which is active species for alkene epoxidation according to the stoichiometric experiments. In order to clearly observe the process, especially the bands at 400 nm and 495 nm, higher concentrations of manganese catalyst and  $H_2O_2$  were applied in Fig. 2b, and the interference in the region from 190 nm to 250 nm was from the absorbance of  $H_2O_2$  (Fig. S7). Noticeably, although the signals at 400 nm and 495 nm was very weak after



Fig. 2. (a) The UV–vis spectra of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  plus  $H_2O_2$  or  $Sc(OTf)_3$ . (b) The UV–vis spectral changes of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  plus  $Sc(OTf)_3$  in the presence of  $H_2O_2$ . Conditions: acetonitrile, 298 K. (a)  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  0.1 mM,  $Sc(OTf)_3$  0.2 mM, NaOTf 0.6 mM,  $H_2O_2$  1 mM; (b)  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  0.15 mM,  $Sc(OTf)_3$  0.3 mM,  $H_2O_2$  3 mM.

the decay within enough reaction time, they still remained detectable, suggesting the three oxygen bridges of  $Mn-(\mu-O)_3$ -Mn cannot be totally dissociated. The UV–vis spectra of dinuclear manganese complex with different Lewis acids in the presence of  $H_2O_2$  were further investigated (Fig. S9-S16). The absorbance reduction at 400 nm and 495 nm from the dissociation of Mn-( $\mu$ -O)<sub>3</sub>-Mn was obviously obtained in the cases of trivalent metal ions, and only slight change was observed in the case of Zn(OTf)<sub>2</sub>. Above results were in agreement with the data from epoxidation reactions. Furthermore, the wavelength of signals remained the same and no obvious shifting was observed in the presence of different Lewis acid. It seems that the non-redox metal ions was not contained in the active species.

The incomplete dissociation of sluggish Mn-( $\mu$ -O)<sub>3</sub>-Mn structure by the addition of high valent non-redox metal ions is also detected in the FT-IR spectra (Fig. 3). The characteristic Mn-O-Mn vibration is observed at 670 cm<sup>-1</sup> and no interference from solvent and Lewis acid exists in this region (Fig. S17) [85,86]. As displayed in Fig. 3, the structure of Mn-( $\mu$ -O)<sub>3</sub>-Mn core remains unchanged in the presence of H<sub>2</sub>O<sub>2</sub>, even in the addition of monovalent metal ion like Na<sup>+</sup>. The signal of Mn-O-Mn at 670 cm<sup>-1</sup> was dramatically weaken, however, still remained observable when Sc(OTf)<sub>3</sub> was added to the dinuclear Mn-( $\mu$ -O)<sub>3</sub>-Mn complex with H<sub>2</sub>O<sub>2</sub>, indicating that the three oxygen bridges of the Mn-( $\mu$ -O)<sub>3</sub>-Mn core was incompletely dissociated.

Non-redox metal ions as Lewis acids influenced the catalytic



Fig. 3. The FT-IR spectra of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  plus  $H_2O_2$  or Lewis acids. Conditions: acetonitrile,  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  10 mM, Sc(OTf)\_3 20 mM, NaOTf 60 mM, H\_2O\_2 100 mM. The black line represents the manganese catalyst in solid state, and other samples are tested in the CH\_3CN solution.

property of [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> through the incomplete dissociation of three oxygen bridges and the formation of catalytically active species. However, the exactly key species was not clear yet, and EPR characterization was conducted to detect the potentially active intermediates. In previous reports, the dinuclear manganese(IV) complex is EPR silent when the typical 16-line signal at g = 2.0 is assigned as the  $\mu$ -oxo-bridged Mn<sub>2</sub>(III,IV) species and the 6-line signal at g = 1.9is assigned as the high-spin mononuclear manganese(II) species (Fig. S18) [74-76,87-90]. The EPR spectra of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ plus  $H_2O_2$  or Sc(OTf)<sub>3</sub> were showed in Fig. 4. The EPR signal was silent when  $H_2O_2$  was added to  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , indicating again that the dinuclear manganese(IV) structure was maintained. The introduction of Sc(OTf)<sub>3</sub> to [Mn<sub>2</sub>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> results in the transformation of EPR spectra from silent to a typical 6-line signal at g = 1.9 corresponding to mononuclear Mn(II) species. It clearly reveals the dissociation of the dinuclear Mn-( $\mu$ -O)<sub>3</sub>-Mn core induced by Sc<sup>3+</sup> and the signal of manganese(II) species is possible from the instability of mononuclear manganese(IV) species, which has not been directly observed in EPR spectra because of its short life and its weakness covered by the strong intensity of mononuclear manganese(II) species [74–76]. The spectrum of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  seems to be complicated in the presence of Sc(OTf)3 and H2O2 and it contains



Fig. 4. The EPR spectra of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  plus  $H_2O_2$  or Sc(OTf)<sub>3</sub>. Conditions: acetonitrile,  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  5 mM, Sc(OTf)<sub>3</sub> 10 mM,  $H_2O_2$  25 mM, 130 K.

**Scheme 2.** Proposed mechanism of olefin epoxidation accelerated by the non-redox metal ions.



signals from mononuclear Mn(II) and dinuclear Mn<sup>III</sup>-O-Mn<sup>IV</sup>. The generation of Mn(II) species may come from the further dissociation of Mn<sup>III</sup>-O-Mn<sup>IV</sup> structure by the affection of Sc(OTf)<sub>3</sub> in the low concentration of H<sub>2</sub>O<sub>2</sub>. Notably, the dinuclear Mn<sup>IV</sup>-O-Mn<sup>IV</sup> species with one oxygen bridge cannot be excluded as the active intermediate because of its silent signal in EPR spectrum.

The electrochemical studies also indicated the interaction between Sc(OTf)<sub>3</sub> and  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ . As shown in Fig. S20, the cyclic voltammogram of [Mn<sub>2</sub><sup>IV</sup>(µ-O)<sub>3</sub>(Me<sub>3</sub>tacn)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> is consistent with the previous reports and the one-electron reduction of [Mn<sub>2</sub><sup>IV</sup>(µ- $O_3(Me_3tacn)_2](PF_6)_2$  is observed at -0.6 V (vs SCE) [6,85]. Undoubtedly, the strong donor properties of the three oxygen bridges cause the decrease of the reduction potential and stabilization of the high-valent  $Mn^{IV}$ -( $\mu$ -O)<sub>3</sub>-Mn<sup>IV</sup> complex. When 10 equiv. of H<sub>2</sub>O<sub>2</sub> as oxidant is added to the dinuclear manganese catalyst, the cyclic voltammogram of  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  remains unchanged and it clearly indicates that the dinuclear structure with three oxygen bridges is maintained in the presence of H<sub>2</sub>O<sub>2</sub>. The addition of Sc(OTf)<sub>3</sub> to  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  in the absence of  $H_2O_2$  gives rise to the mononuclear  $Mn^{II}/Mn^{III}$  couples at +0.74 V (vs SCE). However, as displayed in Fig. S21, adding Sc(OTf)<sub>3</sub> to the dinuclear Mn<sub>2</sub>(IV, IV) complex with 10 equiv. of H<sub>2</sub>O<sub>2</sub> induces the formation of the couple at +1.14 V (vs SCE), which is represented to the couple of dinuclear core Mn<sub>2</sub>(III, IV) to Mn<sub>2</sub>(IV, IV) [75,76]. These results are highly consistent with aforementioned UV-vis, FT-IR and EPR characterizations.

In the previous reports from other groups, the dinuclear  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  was easily synthesized with low concentration of  $H_2O_2$  as oxidant and MnCl<sub>2</sub> as starting material at 273 K [35,83,84]. So we propose that the amount of incompletely dissociated dinuclear manganese species is generally dependent on the amount of  $H_2O_2$ . For instance, when 5 equiv. of  $H_2O_2$  is added to the dinuclear  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , the EPR spectra contains signals from mononuclear Mn(II) and dinuclear  $Mn^{III}$ -O-Mn<sup>IV</sup>. When a large amount of  $H_2O_2$  is applied, such as 300 equiv. of  $H_2O_2$  in the epoxidation reaction, the dinuclear Mn-O-Mn species are easily regenerated from the dissociated mononuclear manganese species or  $Mn^{IV}$ -( $\mu$ -O)<sub>3</sub>-Mn^{IV} cannot be fully dissociated by the affection of Sc(OTf)<sub>3</sub> because of the strong donor properties of the three oxygen bridges.

Taken together the catalytic reaction and characterizations, the possible mechanism of olefin epoxidation in the promotion of the non-redox metal ions was displayed in Scheme 2. The open-loop dinuclear manganese complex, HO-Mn<sup>III</sup>-( $\mu$ -O)-Mn<sup>IV</sup> = O or O = Mn<sup>IV</sup>-( $\mu$ -O)-Mn<sup>IV</sup> = O, was proposed as the active species in the catalytic system based on the following reasons: (1) The active intermediate was generated by the interaction of  $[Mn_2(\mu-O)_3(Me_3tacn)_2](PF_6)_2$  and  $Sc^{3+}$  in the presence of  $H_2O_2$ ; (2) The addition of  $Sc^{3+}$  could crack one or two  $\mu$ -O bridges of  $Mn^{IV}$ -( $\mu$ -O)\_3-Mn^{IV} but at least one  $\mu$ -O bridge was remained, and the diamond structure of Mn-O-Mn core still reserved as the active species in catalytic circle; (3) The signal of dinuclear  $Mn^{III}$ -O-Mn^{IV} complex is detected in EPR experiments; (4)The dinuclear manganese complexes, HO-Mn^{III}-( $\mu$ -O)-Mn^{IV} = O or O = Mn^{IV}-( $\mu$ -O)-Mn^{IV} = O, are established as the active species in the presence of carboxylic acid for alkene epoxidation [2–15]. Certainly, the exact structure of active intermediates need to be further investigated in our next works.

### Conclusions

In summary, this work demonstrated the introduction of non-redox metal ions as Lewis acids to the classic dinuclear manganese complex,  $[Mn_2^{IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , can obviously suppress the catalase-like decomposition of H<sub>2</sub>O<sub>2</sub> and remarkably promote the alkene epoxidation efficiency under mild conditions with H<sub>2</sub>O<sub>2</sub> as the solely terminal oxidant; in particular, the activity improvement is Lewis acidity strength dependent on non-redox metal ions. The novel strategy was successfully applied to the epoxidation reactions of different types of alkenes. Through UV-vis, FT-IR, EPR and CV characterizations, it was evidenced that the trivalent non-redox metal ions as Lewis acids could dissociate one or two  $\mu$ -O bridges of the sluggish dinuclear Mn-( $\mu$ -O)<sub>3</sub>-Mn core and the open-loop dinuclear manganese complex, HO-Mn<sup>III</sup>-( $\mu$ -O)-Mn<sup>IV</sup> = O or  $O = Mn^{IV} - (\mu - O) - Mn^{IV} = O$ , was proposed as the key active species to improve the catalytic efficiency. This work illustrated an alternative protocol of that adding non-redox metal ions to sluggish catalysts can manipulate its reactivity for alkene epoxidation with H<sub>2</sub>O<sub>2</sub> as clean oxidant, and provided clues to understand the role of non-redox metal ions in metalloenzymes and heterogeneous catalysts.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.01.022.

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