

Research paper

Contents lists available at ScienceDirect

# Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

# Bioinspired manganese complex for room-temperature oxidation of primary amines to imines by *t*-butyl hydroperoxide



Lin Lei<sup>a</sup>, Yaju Chen<sup>a,\*</sup>, Zhenfeng Feng<sup>a</sup>, Chunyan Deng<sup>a</sup>, Yepeng Xiao<sup>b</sup>

<sup>a</sup> School of Chemistry, Guangdong University of Petrochemical Technology, Maoming 525000, PR China

<sup>b</sup> School of Chemical Engineering, Guangdong University of Petrochemical Technology, Maoming 525000, PR China

Keywords: Bioinspired metal complex Oxidative coupling Imines Amines TBHP

#### ABSTRACT

A sustainable method is developed for the selective and additive-free synthesis of imines from primary amines with TBHP catalyzed by bioinspired manganese complex (MnCl<sub>2</sub>(TPA)) at room temperature. Use of 0.2 mol % MnCl<sub>2</sub>(TPA) was efficient enough for this transformation by offering excellent conversions up to 98.2% along with 93.4% product yield within 1 h. The influence of reaction parameters (catalyst dosage, solvent, reaction temperature, time, etc.) on the catalytic performance was also investigated in detail. Building on these results, the selected MnCl<sub>2</sub>(TPA) was further employed to transform various primary amines into corresponding imines and exhibited good compatibility even for the challenging aliphatic amine. The high efficiency, combining with a large substrate scope and ambient reaction conditions, makes the developed bioinspired Mn complex/TBHP system a promising pathway to produce imines. This work also paves a way to the expansion of non-heme metal catalysts as efficient platforms for various oxidation reactions.

# 1. Introduction

Imines containing high-activity unsaturated C—N double bonds are among the most significant intermediates for the synthesis of a variety of pharmaceuticals, agrochemicals and molecular motors [1–3]. As a consequence, extensive attention from both academic and industrial field has been attracted toward the synthesis of imines. The condensation reaction between amines and carbonyl compounds is a traditional strategy to acheive imines fabrication. This process involves the use of unstable aldehydes, dehydrating agents and acid catalysts, which restrains its industrial application from the practical and environmental point of view [4]. The direct oxidative coupling of amines to the corresponding imines provides a promising and attractive alternative to the conventional approach.

Over the past decade, considerable efforts have been made for this transformation, thus yielding plentiful catalytic systems based on metal catalysts, such as Cu [2,5,6], Fe [7], Mn [8–10], V [11], Co [12], Pd [13], Au [14], Ru [15], Cd [16], and Ti [17,18]; and other catalysts, such asquinone (TBHBQ) [19], ionic liquids [20], graphene oxide [21], mesoporous carbon [22], and salicylic acid derivative [23]. Despite good catalytic performance, most of theses methodologies involve complicated catalyst preparation process, cumbersome reaction setup,

or harsh reaction conditions, such as high temperature, the addition of oxidative promoters, and light irradiation. For example, a vanadium catalyst (VO(Hhpic)<sub>2</sub>) was developed for the aerobic oxidation of amines to imines at 120 °C in acetonitrile [24]. Liang and co-workers reported salicylic acid complexed with TiO<sub>2</sub> for visible light-driven selective oxidation of amines into imines with air using TEMPO as a co-catalyst [18]. Moreover, some reported protocols are often limited in lower activity and unruly selectivity for aliphatic amines [25]. In view of the above, the exploration of simple catalytic system with high efficiency and good substrate expansibility for the oxidative coupling of amines under mild even ambient conditions is highly desirable.

Catalytic oxidation methodologies based on bioinspired metal complexes and peroxides, which can be regarded as biologically inspired, are gradually highlight their remarkable advantages of mild reaction conditions, excellent reactivity and high selectivity [26,27]. Among them, the biologically important elements-based complexes such as iron and manganese attract particular attention. Iron porphyrins, as the mimics of the cytochrome P450 active site, has been the most extensively studied in various oxidation reactions. For eaxmple, fluorinated Fe-porphyrins were found to be highly efficient for catalyzing the double epoxidation of divinylbenzene with  $H_2O_2$  under mild conditions [28]. Metal complexes with porphyrin-inspired tetradentate nitrogen (N<sub>4</sub>) ligands

\* Corresponding author. E-mail address: chenyaju970@126.com (Y. Chen).

https://doi.org/10.1016/j.ica.2021.120282

Received 19 January 2021; Received in revised form 30 January 2021; Accepted 31 January 2021 Available online 9 February 2021 0020-1693/© 2021 Elsevier B.V. All rights reserved.



**Scheme 1.** Room-temperature oxidation of primary amines to imines catalyzed by non-heme metal complexes.

known as non-heme metal complexes possess of particular appeal because of their fine tunable and easily variable structural and electronic properties comparing to heme (porphyrin)-based catalysts [29,30]. Talsi and coworkers reported Fe and Mn aminopyridine catalysts for the olefin epoxidations with H2O2/carboxylic acid with high efficiency (up to 1000 turnover number (TON)) and selectivity (up to 100%) [31]. Over the past decades, Que [27,32] and Nam [33] have made significant efforts to achieve abiological oxidation reactions with non-heme Fe (Mn)/peroxides catalytic systems and reveal their catalytic mechanism. Romero and Rodríguez have also developed a series of catalytic systems based on non-heme metal complexes for alkene epoxidation [34-38]. Despite significant progress, most of these studies focused on olefin epoxidation and alkane hydroxylation reactions. Given the importance of oxidative coupling of amines to imines, this transformation has been actively pursued, but non-heme Fe(Mn)/peroxides catalytic systems for this reaction exhibiting high reactivity and working under a green process remain scarce.

In this contribution, we developed a facile and sustainable protocol based non-heme metal catalysts bearing TPA (tris(2-pyridylmethyl)-amine) employing TBHP (*t*-butyl hydroperoxide) as an oxidant for the selective synthesis of imines from amines (Scheme 1). It was found that  $MnCl_2(TPA)$  was the optimal catalyst. Reactions were performed in short reaction times at low catalysts loading (0.2 mol %). The remarkably high conversion of benzylamine (98.2%) was obtained with 93.4% yield for benzylidenebenzylamine within 1 h at room temperature (30 °C). Further, various amines are smoothly converted into the desired imines in good yields (up to 99.0%) with high selectivity under optimal reaction conditions. The observed excellent performace provided a promising methodology based on no-heme Mn/TBHP system to offer various valuable imines under a sustainable way.

## 2. Experimental section

# 2.1. Materials

2-(Aminomethyl)pyridine (purity, 99%) and 2-(chloromethyl)pyridine hydrochloride (purity, 97%) were purchsed from J&K Scientific Ltd. All primary amines (purity, >97%), metal salts (purity, >98%), benzylidenebenzylamine (purity, 99%), *t*-butyl hydroperoxide (TBHP,

# Table 1

Oxidative coupling of benzylamine catalyzed by various non-heme metal com-

plexes. <sup>[a]</sup> (	Mn(TPA)Cl <sub>2</sub>	$\stackrel{\text{HP}}{\longrightarrow} \qquad \qquad$	
Entry	Catalyst	Conversion <sup>[b]</sup> (%)	Yield <sup>[b]</sup> (%)
1	-	5.4	3.1
2	CoCl <sub>2</sub> (TPA)	23.8	21.3
3	NiCl <sub>2</sub> (TPA)	22.0	18.9
4	CuCl <sub>2</sub> (TPA)	34.5	32.2
5	ZnCl <sub>2</sub> (TPA)	24.0	20.5
6	FeCl <sub>3</sub> (TPA)	95.8	87.5
7	MnCl <sub>2</sub> (TPA)	98.2	93.4
8	MnBr <sub>2</sub> (TPA)	96.8	89.6
9	Mn(ClO <sub>4</sub> ) <sub>2</sub> (TPA)	96.4	89.0

<sup>[a]</sup> Reaction conditions: 1a (1.0 mmol), TBHP (2.0 mmol), catalyst (0.2 mol%), acetonitrile (5 mL), room temperature (30 °C), 1 h.

<sup>[b]</sup> Conversion and yield determined by GC of the crude reaction mixture using naphthalene as the internal standard.

70% aq.), cumene hydroperoxide (CHP, purity 80%), and ureahydrogen peroxide (UHP, purity 98%) were obtained from Energy Chemical and TCI. Hydrogen peroxide ( $H_2O_2$ , 30% aq.) and other commercially available chemicals (analytical grade) were available from local suppliers.

# 2.2. Characterization

Solution NMR spectra were recorded with a Bruker Avance III HD 400 MHz spectrometer at ambient temperature in deuterated chloroform (CDCl<sub>3</sub>) using TMS as an internal standard. Elemental analysis of C, H, and N was performed on a Vario EL cube instrument. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were obtained under ambient conditions at a resolution of 4 cm<sup>-1</sup> in the wave number range of 4000–400 cm<sup>-1</sup> by using an EQUINOX 55 spectrometer. Mass spectrometry analyses were recorded in a Shimadzu LC-MS 2010 liquid chromatography-tandem mass spectrometry (ESI-MS in methanol) with negative mode. The ultra-violet-visible light (UV-vis) spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The solution of samples in dichloromethane (ca. 1.0 mM) was poured into a 1 cm quartz cell for UV-vis spectroscopy with dichloromethane as the reference. Gas chromatographic (GC) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a flame ionization detector and a capillary column (Rtx-5, 30 m  $\times$  0.32 mm  $\times$  0.25 mm).

#### 2.3. Synthesis of TPA and non-heme metal complexes

TPA,  $[MnX_2(TPA)](X = Cl, Br, ClO_4)$ ,  $[FeCl_3(TPA)]$ ,  $[CoCl_2(TPA)]$ ,  $[NiCl_2(TPA)]$ ,  $[CuCl_2(TPA)]$  and  $[ZnCl_2(TPA)]$  were synthesized according to published procedures [39–42], and the synthetic procedure routes of them were outlined in Scheme 2. Further details of these materials are given in the Supplementary Information.

# 2.4. Catalyst testing

All the oxidative coupling reactions of amines were conducted in a



Scheme 2. Synthetic route for the non-heme metal complexes.

#### Table 2

The results of the benzylamine oxidative coupling reaction in different solvent catalyzed by  $MnCl_2(TPA)$ .<sup>[a]</sup>

Entry	Solvent	Conversion <sup>[b]</sup> (%)	Yield <sup>[b]</sup> (%)
1	water	53.5	42.6
2	methanol	80.6	67.4
3	acetonitrile	98.2	93.4
4	dichloromethane	62.8	51.8
5	toluene	22.5	19.3
6	cyclohexane	25.2	20.1

 $^{[a]}$  Reaction conditions: benzylamine (1.0 mmol), TBHP (2.0 mmol), catalyst (0.2 mol%), 30  $^\circ C$ , 1 h.

<sup>[b]</sup> The same as Table 1.

25 mL round-bottom flask. Typically, benzylamine (1 mmol), TBHP (2 mmol), and catalyst (0.2 mol%, bsed on the mol of benzylamine) in CH<sub>3</sub>CN (5 mL) were quickly added into the flask. Then, the reaction mixture was stirred at room temperature (30 °C). After reaction, 2–3 drops of reaction mixture were added to 2 mL acetonitrile, and dried by anhydrous magnesium sulfate. The product was analyzed by GC using a Shimadzu GC 2010 gas chromatograph equipped with a flame ionization detector and a capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 mm). The conversion and selectivity were determined using the calibration curves obtained with naphthalene as an internal standard and each authentic imine product. All reactions were repeated at least three times, and the average values were used.

#### 3. Results and discussion

The oxidative coupling of benzylamine (**1a**) with TBHP in acetonitrile was chose as a model reaction to evaluate the catalytic performance of as-perpared non-heme metal complexes. The results were listed in the Table 1.

First, the control experiment was carried out at 30 °C in the absence of any catalyst, giving a negligible yield of 3.1% to benzylidenebenzylamine (**2a**) within 1 h (Table 1, entry 1). Then, several metal comlexes including CoCl<sub>2</sub>(TPA), NiCl<sub>2</sub>(TPA), CuCl<sub>2</sub>(TPA), ZnCl<sub>2</sub>(TPA), FeCl<sub>3</sub>(TPA) and MnCl<sub>2</sub>(TPA) were examined under the same reaction conditions (Table 1, entries 2 ~ 7). It was found that MnCl<sub>2</sub>(TPA) and FeCl<sub>3</sub>(TPA) showed highly effective of these, and gave a good yields of 87.5 and 93.4% to **2a**, respectivly (Table 1, entries 6 and 7). Besides, the catalytic activity of manganese complexes was not very sensitive to the anions of these catalyts, such as Cl<sup>-</sup>, Br<sup>-</sup> and (ClO<sub>4</sub>)<sup>-</sup>, and the cooresponding complexes exhibited satisfactory performance (Table 1, entry 7 ~ 9). Benzaldehyde is the main by-product in this transformation.

Moreover, various solvents, such as water, acetonitrile, methanol, dichloromethane, toluene, and cyclohexane were explored in the oxidative coupling reaction of benzylamine in different solvent catalyzed by MnCl<sub>2</sub>(TPA). As listed in Table 2, the catalytic activity strongly influenced by the solvent polarity. Water, known as the strong polar green solvent, has been attracted continuous attention in some organic reactions. This transformation could proceed in water with a moderate conversion (Table 2, entry 1). When the slightly lower polarity methanol was used, the catalytic activity was obviously increased to give a 80.6% conversion (Table 2, entry 2). This probably due to strong interaction between the solvent and the metal center of catalyst, suppressing the ability of the formation of the active high-valence metal species in the oxidative progress [43]. Nearly complete conversion of benzylamine to the imine was observed in acetonitrile (Table 2, entry 3). Decreasing the polarity of the solvent showed a decrease in the conversion to benzylamine (Table 2, entry 4  $\sim$  6). The lower activity in nonpolar solvents may be attributed to the limited compatibility of the benzylamine and catalyst in the aqueous solution of the oxidant [44].

To standardize the oxidant needed for this reaction, common terminal oxidants, including aqueous hydrogen peroxide ( $H_2O_2$ ), *t*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP) and urea-



**Fig. 1.** Effect of oxidant on benzylamine oxidative coupling reaction (Reaction conditions: benzylamine (1.0 mmol), oxidant (2.0 mmol),  $MnCl_2(TPA)$  (0.2 mol %), acetonitrile (5 mL), 30 °C, 1 h).



**Fig. 2.** Effect of the catalyst dosage (A), TBHP dosage (B), reaction temperature (C) and time (D) on catalytic performance of  $MnCl_2$ (TPA) (a: conversion; b: selectivity). Reaction conditions: (A) benzylamine (1 mmol), TBHP (2 mmol), 30 °C, 1 h; (B)  $MnCl_2$ (TPA) (0.2 mol%), benzylamine (1 mmol), 30 °C, 1 h; (C)  $MnCl_2$ (TPA) (0.2 mol%), benzylamine (1 mmol), TBHP (2 mmol), 1 h; (D)  $MnCl_2$ (TPA) (0.2 mol%), benzylamine (1 mmol), TBHP (2 mmol), 30 °C.

hydrogen peroxide (UHP) and were investigated. As shown in Fig. 1, Use of  $H_2O_2$  as an oxidant gave relatively poor conversion of 18.2% with a selectivity of 81.7%. During this reaction process,  $H_2O_2$  was decompounded rapidly with the observation of generation of oxygen bubbles, thereby reducing the oxidization capability. Further, high conversions (>92.2%) of amine with good selectivities (90.0%) of desired imine were achieved by using other organic oxidants (TBHP, CHP and UHP). In particular, a complete conversion of benzyl amine to the imine was observed in the presence of TBHP. Therefore, we selected TBHP as the oxidant in the following studies. Moreover, a reaction carried out under N<sub>2</sub> atmosphere yielded only traces of the desired imine demonstrating the necessity for oxidizing conditions in this transformation.

To screen the optimal reaction conditions for this transformation, the effect of various reaction parameters (catalyst dosage, TBHP dosage, temperature and time) was investigated in detail and the results were summarized in Fig. 2. First, the influence of the dosage of  $Mn(TPA)_2$  was studied as represented in Fig. 2A. The higher activity of the catalyst was observed with the increasing amount of catalyst from 0.1 to 0.2 mol% where the benzylamine conversion increased from 62.2 to 98.3% with a selectivity of 95.1%. A further increase in catalyst mount to 0.3 mol% had little effect on conversion and selectivity, while the use of 0.35 mol% led to a clear decrease in both conversion and selectivity. Similarly, a



Scheme 3. Oxidation of various primary amines to imines catalyzed by MnCl<sub>2</sub>(TPA) (the conversion and selectivity (in parenthesis) were determined by GC; reaction conditions: benzylamine (1.0 mmol), TBHP (2.0 mmol), catalyst (0.2 mol%), 30 °C, 1 h).

increasing dosage of oxidant TBHP promoted the conversion of benzylamine in a certain range, while the selectivity decreased with further increase of TBHP amount as the amount exceeds 2 mol (Fig. 2B). It could be clearly observed that the reaction temperatture showed a strong effect on this reaction (Fig. 2C). With the rise of temperature from 10 to 30 °C, the benzylamine conversion enhanced sharply from 31.7 to 98.2%, and the temperature showed slightly negative influence on the desired imine selectivity beyond 30 °C. Furthermore, the reaction profile of MnCl<sub>2</sub>(TPA) with time is shown in Fig. 2D. The benzylidenebenzylamine synthesis from benzylamine with TBHP proceeded rapidly, and more than 98.2% benzylamine comversion was obtained within 60 min at 30 °C. During the whole process, the benzylidenebenzylamine selectivity remains as high as >95.1%. The benzylidenebenzylamine yield experienced a continuing growth up to 99.0% with a slightly decreased selectivity of 92.1% within 75 min. Considering the yield of desired product, the optimal reaction time can be locked at 60 min in this reaction.

Consequently, the optimal reaction conditions for the oxidative coupling reaction was identified as: benzylamine (1 mmol),  $MnCl_2(TPA)$  (0.2 mol%) and TBHP (2 mmol) in acetonitrile at 30 °C for 1 h.

With the optimal reaction conditions obtained, we inwestigated the general applicability of the catalyst MnCl<sub>2</sub>(TPA) using various aromatic amines with either electron-donating or electron-withdrawing substituents and aliphatic amines as substrates. As summarized in Scheme 3, all the above amines could be smoothly oxidized by MnCl<sub>2</sub>(TPA) to the corresponding imines in good yields (76.5~>99.0%) and excellent selectivity (>91.0%). Clearly, the catalytic performance for this oxidative coupling reaction was modest influenced by electronic properties of the substituents on phenyl ring (Scheme 3, 1a-1f), indicating the good tolerance of functional-groups. With the increase of electronwithdrawing property of the substituent, the corresponding imine was obtained in a relatively lower yield (2d vs. 2e vs. 2f). However, with the increasing of steric hindrance of substituents (1g and 1h), apparently lower conversion of the related product was obtained under the same conditions. For  $\alpha$ -methyl benzylamine (1h), long reaction time (3.0 h) was required to achieve higher conversion (87.0%). Notably, heteroaromatic amine (2i aand 2j) were also suitable substrates in this transformantion, affording the desired products with high efficiency. In terms of aliphatic amines 1k and 1i, which might show inertness to the oxidation reaction, can also provide a good coversion with high selectivity by prolonging the reaction time. These results indicate the developed catalyytic protocol shows wide substrate scope for this amine oxidative coupling reaction.

# 4. Conclusions

In summary, a series of bioinspired metal complexes bearing TPA ligands were firstly employed for the oxidative coupling of primary amines to imines. These complexes showed high-efficiency and selectivity in this transformation by using aqueous TBHP as an oxidant at room temperature under additive-free conditions. Especially, at a low catalyst loading (0.2 mol %) of MnCl<sub>2</sub>(TPA), a 98.2% conversion of benzylamine with 93.4% yield to benzylidenebenzylamine were obtained within 1 h. Under the optimal reaction conditions, MnCl<sub>2</sub>(TPA) presented a wide substrate scope to give the desired products in 70.9  $\sim$  96.2% yields. Particularly, 1-heptylamine, a challenging aliphatic amine, was also amenable to this protocol and gave a good selectivity of 92.7%. This work provides a sustainable approach to the oxidative synthesis of imines from amines. Further investigations are underway to elucidate the reaction mechanism and expand application of the catalyst to other oxidation reactions.

# CRediT authorship contribution statement

Lin Lei: Investigation, Data curation, Writing - original draft, Writing - review & editing. Yaju Chen: Conceptualization, Writing - review & editing, Supervision, Resources, Validation. Zhenfeng Feng: Investigation, Methodology. Chunyan Deng: Formal analysis, Software. Yepeng Xiao: Visualization, Project administration.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

This work was financially supported by the Guangdong Basic and Applied Basic Research Foundation (2019A1515010612), Characteristic Innovation Project of Guangdong Ordinary University (2019KTSCX107), Science and Technology Plan of Maoming (2020509), Guangdong University of Petrochemical Technology Scientific Research Foundation (2019rc049, 2018rc53).

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120282.

# References

- [1] B. Chen, L. Wang, S. Gao, ACS Catal. 5 (2015) 5851–5876.
- [2] M. Largeron, M.-B. Fleury, Angew. Chem. Int. Ed. 51 (2012) 5409–5412.
- [3] L. Greb, J.M. Lehn, J. Am. Chem. Soc. 136 (2014) 13114–13117.
- [4] S. Biswas, B. Dutta, K. Mullick, C.-H. Kuo, A.S. Poyraz, S.L. Suib, ACS Catal. 5 (2015) 4394–4403.
- [5] Z.-Y. Zhai, X.-N. Guo, G.-Q. Jin, X.-Y. Guo, Catal. Sci. Technol. 5 (2015) 4202–4207.
- [6] K. Marui, A. Nomoto, M. Ueshima, A. Ogawa, Tetrahedron Lett. 56 (2015) 1200–1202.
- [7] M. Deb, S. Hazra, P. Dolui, A.J. Elias, ACS Sustainable Chem. Eng. 7 (2018) 479–486.
- [8] X.-T. Zhou, Q.-G. Ren, H.-B. Ji, Tetrahedron Lett. 53 (2012) 3369–3373.
- [9] Z. Zhang, F. Wang, M. Wang, S. Xu, H. Chen, C. Zhang, J. Xu, Green Chem. 16 (2014) 2523–2527.
- [10] Y.Y. Zhang, Y.Y. Fang, X.Z. Wang, Y.Q. Chen, L.Y. Dai, J. Chem. Eng. Chinese Universities 34 (2020) 110–115.
- [11] L. Wang, B. Chen, L. Ren, H. Zhang, Y. Lü, S. Gao, Chin. J. Catal. 36 (2015) 19–23.
  [12] J. Long, K. Shen, Y. Li, ACS Catal. 7 (2016) 275–284.
- [13] S. Furukawa, A. Suga, T. Komatsu, Chem. Commun. 50 (2014) 3277-3280.
- [14] H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li, F. Wang, ACS Catal. 7 (2017) 3632–3638.
- [15] H.A. Ho, K. Manna, A.D. Sadow, Angew. Chem. Int. Ed. 51 (2012) 8607-8610.
- [16] Y. Xu, Y. Chen, W.-F. Fu, Appl. Catal. B 236 (2018) 176–183.
- [17] Z. Wang, X. Lang, Appl. Catal. B 224 (2018) 404–409.
- [18] X. Li, H. Xu, J.-L. Shi, H. Hao, H. Yuan, X. Lang, Appl. Catal. B 244 (2019) 758-766.

- [19] A.E. Wendlandt, S.S. Stahl, Org. Lett. 14 (2012) 2850-2853.
- [20] A. Monopoli, P. Cotugno, F. Iannone, F. Ciminale, M.M. Dell'Anna, P. Mastrorilli, A. Nacci, Eur. J. Org. Chem. 2014 (2014) 5925–5931.
- [21] H. Huang, J. Huang, Y.-M. Liu, H.-Y. He, Y. Cao, K.-N. Fan, Green Chem. 14 (2012) 930–934.
- [22] B. Chen, L. Wang, W. Dai, S. Shang, Y. Lv, S. Gao, ACS Catal. 5 (2015) 2788–2794.
   [23] C.P. Dong, Y. Higashiura, K. Marui, S. Kumazawa, A. Nomoto, M. Ueshima,
- A. Ogawa, ACS Omega 1 (2016) 799–807.
- [24] S. Kodama, J. Yoshida, A. Nomoto, Y. Ueta, S. Yano, M. Ueshima, A. Ogawa, Tetrahedron Lett. 51 (2010) 2450–2452.
- [25] M. Largeron, Eur. J. Org. Chem. 2013 (2013) 5225-5235.
- [26] O. Cusso, M. Cianfanelli, X. Ribas, R.J. Klein Gebbink, M. Costas, J. Am. Chem. Soc. 138 (2016) 2732–2738.
- [27] L. Que Jr, W.B. Tolman, Nature 455 (2008) 333–340.
   [28] K. Zhang, Y. Yu, S.T. Nguyen, J.T. Hupp, L.J. Broadbelt, O.K. Farha, Ind. Eng. Chem. Res. 54 (2015) 922–927.
- [29] A. Fingerhut, O.V. Serdyuk, S.B. Tsogoeva, Green Chem. 17 (2015) 2042–2058.
- [30] G. Mukherjee, C.V. Sastri, Israel J. Chem. 60 (2020) 1032–1048.
- [31] O.Y. Lyakin, R.V. Ottenbacher, K.P. Bryliakov, E.P. Talsi, ACS Catal. 2 (2012) 1196–1202.
- [32] S. Kal, S. Xu, L. Que Jr., Angew. Chem. Int. Ed. 59 (2020) 7332–7349.
- [33] J. Chen, Z. Jiang, S. Fukuzumi, W. Nam, B. Wang, Coordin. Chem. Rev. 421 (2020), 213443.
- [34] E. Manrique, X. Fontrodona, M. Rodríguez, I. Romero, Eur. J. Inorg. Chem. 2019 (2019) 2124–2133.
- [35] J. Rich, M. Rodríguez, I. Romero, X. Fontrodona, P.W.N.M. van Leeuwen, Z. Freixa, X. Sala, A. Poater, M. Solà, Eur. J. Inorg. Chem. 2013 (2013) 1213–1224.
- [36] J. Rich, E. Manrique, F. Molton, C. Duboc, M.-N. Collomb, M. Rodríguez, I. Romero, Eur. J. Inorg. Chem. 2014 (2014) 2663–2670.
- [37] J. Rich, M. Rodriguez, I. Romero, L. Vaquer, X. Sala, A. Llobet, M. Corbella, M. N. Collomb, X. Fontrodona, Dalton Trans. (2009) 8117–8126.
- [38] E. Manrique, A. Poater, X. Fontrodona, M. Sola, M. Rodriguez, I. Romero, Dalton Trans. 44 (2015) 17529–17543.
- [39] B.-K. Shin, Y. Kim, M. Kim, J. Han, Polyhedron 26 (2007) 4557-4566.
- [40] Z. He, D.C. Craig, S.B. Colbran, J. Chem. Soc., Dalton Trans. (2002) 4224-4235.
- [41] Y. Liu, R. Xiang, X. Du, Y. Ding, B. Ma, Chem. Commun. 50 (2014) 12779–12782.
- [42] A.L. Ward, L. Elbaz, J.B. Kerr, J. Arnold, Inorg. Chem. 51 (2012) 4694-4706.
- [43] R. Luo, R. Tan, Z. Peng, W. Zheng, Y. Kong, D. Yin, J. Catal. 287 (2012) 170–177.
- [44] Y. Chen, R. Tan, Y. Zhang, G. Zhao, W. Zheng, R. Luo, D. Yin, Appl. Catal. A 491 (2015) 106–115.