

Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Yang, H. Du, J. Liu, Z. zhou, X. Hu and Z. Zhang, *Green Chem.*, 2016, DOI: 10.1039/C6GC02186G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/green-chem

YAL SOCIETY CHEMISTRY

Green Chemistry

ARTICLE

Received 00th August 2016, Accepted 00th August 2016

DOI: 10.1039/x0xx00000x

www.rsc.org/

Oxidation of olefins using molecular oxygen catalyzed by part-permillion level of recyclable copper catalyst under mild conditions

Guoqiang Yang, Huiyuan Du, Jia Liu, Zheng Zhou, Xingbang Hu*, Zhibing Zhang*

Copper catalyst with an imidazole salt tag ([Cu-Imace-R-H][X], $X=F^{-}$, CI^{-} , Br^{-} , I^{-} , $CF_{3}CO_{2}^{-}$, HSO_{4}^{-} , NO_{3}^{-} , PF_{6}^{-} , or BF_{4}^{-} ; R=H or CH₃) show quite high reactivity for the oxidation of nonaromatic olefins with good selectivity to the epoxides. The reactions perform well at part-per-million (ppm) catalyst loading under mild temperature and ambient pressure. The highest turn over frequency (TOF) could reach up to 900000 h⁻¹. The catalytic activity are easy to be controlled by changing the anion of [Cu-Imace-R-H][X]. This catalyst is effective for a series of substrates, include internal and terminal olefins, triand tetra-substituted olefins, aromatic olefins. In addition, the copper catalyst can be conveniently separated from the reaction system and reused for at least six cycles without obvious loss of catalytic activity.

Introduction

Oxidation of olefins is a dominant reaction both in industrial and academia, because the epoxides have been widely used in the production of epoxy resins, paints, surfactants, and so on. Besides, they are highly valued as synthetic intermediates in the industrial processes¹⁻⁶. Thus, the development of effective methods for the selective oxidation of olefins has drawn much attention over the past several years¹⁻⁸.

Various oxygen donors such as oxone⁷, sodium hypochlorite⁸, sodium periodate⁹, iodosylbenzene^{10, 11}, tertbutyl hydroperoxide¹²⁻¹⁴, hydrogen peroxide¹⁴⁻¹⁸ and urea hydrogen peroxide^{19, 20} have been used in the catalytic oxidation of olefins. As an oxidant, molecular oxygen is cheap, clean, readily available, and environmentally friendly²¹. However, it is relatively unreactive toward the strong C-H and C=C bond unless it is activated by highly efficient catalysts^{22, 23}. Otherwise, high reaction temperature or pressure are required, which is against to the general requirement of green chemistry. Many catalysts have been developed for the epoxidation of olefins with molecular oxygen as oxidant, such as metalloporphyrins²²⁻³³, metal phthalocyanines³⁴, transition metals oxides³⁵, salen-metal complexes³⁶⁻⁴⁰, heteropoly acid^{41,} ⁴² and so on⁴³⁻⁴⁵. Among these catalysts reported, metalloporphyrins which are the mimics of the Cytochrome

P450 active site represent the most effective one²²⁻³¹. The high reactivity of metalloporphyrins can greatly reduce the loading amount of catalyst, and the concentration of metalloporphyrins used in the oxidations can be as low as partper-million (ppm) level (for examples, ratio of catalyst to substrate: 0.1 ppm⁴⁶,100 ppm⁴⁷, 500 ppm²⁵, 1000 ppm²⁶). Although metalloporphyrins show high catalytic activity, their preparation processes are complicated and need to consume large amounts of organic solvents²²⁻³¹.

We have developed a series of effective catalysts modified by ionic tags for the oxidation reaction⁴⁸⁻⁵¹. Among these compounds, the synthesis of the copper catalyst with an imidazole salt tag are very simple and environmentally friendly⁴⁹. The whole synthesis process of this catalyst performs quite well in water (Scheme 1). Herein, we found that these [Cu-Imace-R-H][X] catalysts are super reactive for the oxidation of olefins. 1ppm of catalyst can well promote the epoxidation under mild condition. Besides, this catalyst is easy to be separated and reused without obvious loss of efficiency.



(X = F, Cl, Br, I, CF₃CO₂, HSO₄, NO₃, PF₆, or BF₄; R=H or CH₃)

. 20000x

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China. Fax: +86 2583 336599; Tel: +86 2583 596665; E-mail: huxb@niu.edu.cn: zbzhana@niu.edu.cn

⁺ Electronic Supplementary Information (ESI) available: Experimental details and characterization results (GC- MS). See DOI: 10.1039/x0xx00000x

Page 2 of 8

Green Chemistry

ARTICLE

Table 1 The performance of different catalysts. ^a						
		- (-1)	Selectivity (%) ^b			
Entry	Catalyst	Conv. (%)	СНО	Cyol	Cyone	
1	[Cu-Imace-H-H][F]	41	83	4	10	
2	[Cu-Imace-H-H][Cl]	43	82	4	11	
3		(96)	(76)	(4)	(14)	
4	[Cu-Imace-H-H][Br]	50	82	4	10	
5		(98)	(75)	(4)	(17)	
6	[Cu-Imace-H-H][I]	56	81	5	9	
7		36	81	4	13	
8		(97)	(80)	(3)	(11)	
9	[Cu-Imace-H-H][HSO ₄]	23	84	2	12	
10		(92)	(82)	(3)	(11)	
11	[Cu-Imace-H-H][CF ₃ CO ₂]	18	81	6	8	
12	[Cu-Imace-H-H][PF ₆]	53	87	2	10	
13	[Cu-Imace-H-H][BF ₄]	60	84	3	9	
14		(96)	(82)	(2)	(9)	
15	[Cu-Imace-CH ₃ -H][Cl]	45	81	5	13	
16	[Cu-Imace-H-CH ₃][I]	17	80	6	11	
17	[Imace-H-H][BF ₄]	2	88	1	10	
18	[Cu-Imace-H-H][BF ₄]+	62	81	1	10	
	[Imace-H-H][BF ₄]	05				
19	Cu(AcO) ₂	37	72	4	13	
20	Cu(CF ₃ COO) ₂	28	82	4	10	
21	Cu(acac) ₂	17	80	3	11	

^a Reaction condition: cyclohexene (0.2mol), CH_3CN (50mL), isobutyraldehyde (0.2mol), and catalyst-to-substrate molar ratios is $1:10^6$ (1ppm), temperature: 60 °C, O_2 bubbling (1atm), reaction time: 3 hours. Values in parentheses were obtained with 800 ppm catalyst in 6 hours. The products were analysed by GC and GC-MS. ^b The selectivity were determined by GC using o-dichlorobenzene as internal standard. Selectivity = (the yield of target product)/(the conversion of reactant)×100%.



Scheme 2 The oxidative transformations of cyclohexene

Results and discussion

Cyclohexene epoxidation catalyzed by catalysts with different anions

Eleven simple copper catalysts with an imidazole salt tag ([Cu-Imace-R-H][X], X'=F', Cl', Br', I', CF₃CO₂', HSO₄', NO₃', PF₆', or BF₄'; R=H or CH₃) were synthesized according to the our previous report (See ESI for details)⁴⁹. The oxidation of cyclohexene catalysed by [Cu-Imace-R-H][X] was selected as a probe to investigate the activity of these catalysts. Under the reaction conditions investigated, the oxidation of cyclohexene

mainly produced epoxycyclohexane (CHO) with a little of 2cyclohexen-1-ol (Cyol) and 2-cyclohexen-1-one (Cyone) (Scheme 2). The byproducts include 1,2-cyclohexanediol, 2,3epoxycyclohexanol, 2,3-epoxycyclohexanone based on GC-MS analysis. Besides, there has less than 1% nonvolatile byproducts which may be oligomers and polymers. Using 1 ppm catalysts, the reaction can almost complete in 10 hours under mild condition (Fig. 1).

The conversions of cyclohexene range from 17 to 60% by using [Cu-Imace-R-H][X] with different anions after 3h (Table 1). It suggests that the reactivity of these catalysts can be easy controlled by introducing different anion. Changing the anion can induce the electron rearrangement on the active metal and results in catalysts with diverse reactivity^{48, 50}. It is interesting to find that, for the catalysts modified by halogen anion, their catalytic reactivity increase in the following order I >Br >Cl >F. Among these four anions, F has strongest electron withdrawing ability, whereas I is the weakest one. This observation further proves our previous theoretic results

Published on 02 November 2016. Downloaded by Ryerson Polytechnic University on 03/11/2016 02:09:44.

Journal Name

about the relation between the electron affinity and catalytic activity of these catalysts modified by ionic tags ⁵⁰. Inspiring by this idea, the catalysts modified by weakly coordinating anions BF_4^- and PF_6^- were synthesized. It is exciting to find that these two catalysts show quite higher catalytic reactivity (Entries 12 and 13, Table 1). At the same time, [Cu-Imace-H-H][PF₆] give the highest CHO selectivity.



Fig. 1. Profile of the conversion of cyclohexene oxidation using different amounts of [Cu-Imace-H-H][BF₄] (catalyst-to-substrate molar ratios, ppm): substrate (0.2mol), isobutyraldehyde (0.2mol), CH₃CN (50mL), O₂ bubbling(1 atm), 60 $^{\circ}$ C.



Fig. 2. The product selectivity of cyclohexene epoxidation using different amounts of $[Cu-Imace-H-H][BF_4]$ (Reaction time: 3h).

To further understand the catalytic ability of these copper catalyst with an imidazole salt tag. $Cu(OAc)_2$, $Cu(O_2CCF_3)_2$ and $Cu(acac)_2$ were used as bench mark under the optimum conditions (Entries 19-21, Table 1). The catalytic reactivity of these three compounds is lower than that of [Cu-Imace-H-H][BF₄]. Besides, the selectivity of $Cu(OAc)_2$ is not good. To eliminate the possibility of a Cu-carbene system serving as catalyst, the hydrogen of C_2 -H was replaced by methyl and a methylated catalyst [Cu-Imace-CH₃-H][CI] was synthesized. The catalytic ability of [Cu-Imace-CH₃-H][CI] is quite similar to that of [Cu-Imace-H-H][CI] (Entries 2 and 15, Table 1). It suggests that the active center is the copper chelated by carboxylic acid.

The trace [Imace-R-H][X] residual in the [Cu-Imace-R-H][X] compound cannot assist the reaction because the catalytic reactivity of [Cu-Imace-H-H][BF₄]+[Imace-H-H][BF₄] is almost the same to that of [Cu-Imace-H-H][BF₄] (Entries 13 and 18, Table 1). Further more, almost no reaction happens when using [Imace-H-H][BF₄] alone (Entry 17).

To explore the role of the active N-H part in [Cu-Imace-R-H][X], a N-methylation catalyst [Cu-Imace-H-CH₃][I] was synthesized according the procedure reported in the ESI. It is interesting to find that the catalytic ability of [Cu-Imace-H-CH₃][I] is obviously lower than these of [Cu-Imace-H-H][I] and [Cu-Imace-H-H][BF₄] (Entries 6, 13 and 16, Table 1). However, almost no reaction happens when [Imace-H-H][BF₄] was used without the present of cooper (Entry 17). It suggests that the active N-H can assist the active center copper promote the reaction.

Among the catalysts investigated here, $[Cu-Imace-H-H][BF_4]$ is the best choice from the viewpoint of reactivity and CHO selectivity. This compound was used for further investigation.

Cyclohexene oxidation catalyzed by trace amount of catalyst (ppm level)

It is exciting to find that [Cu-Imace-H-H][BF₄] is super active so that the cyclohexene epoxidation can perform quite well at ppm catalyst loading (Fig. 1). The conversion of cyclohexene can reach 90% in 10 hours promoted by 0.1ppm [Cu-Imace-H-H][BF₄] under mild condition, and the corresponding turn over frequency (TOF) value is 900000 h⁻¹. It is worth noticing that almost no reaction happens (conversion < 2%) without catalyst at the same temperature and O₂ pressure. When the concentration of catalyst was increased to 1ppm, the conversion of cyclohexene can reach almost 100% in 10 hours (TOF: 100000h⁻¹).

No matter how much catalyst was used, the total selectivity of CHO, Cyol and Cyone is larger than 94% with a preference to the epoxide CHO (Fig. 2). Low concentration of catalyst is benefit for the produce of the epoxide. A slight decrease of the CHO selectivity was observed as the increasing of catalyst loading from 0.1 to 10 ppm.

Indeed, both the concentration and anions of the catalyst have influence on the reaction selectivity. Many investigators reported the epoxidation involves a free-radical process^{21, 41, 52,} ⁵³. Previous researches have shown that halogen anions (Cl and Br) can react with the radical to produce a halogenintermediate which can be further oxidized to produce deep oxidation products⁵⁴. High catalyst concentration is favourable for the collision between radical and anion. When the concentration of catalyst was increased to 800 ppm, catalysts with Cl⁻ and Br⁻ as anion show lower CHO selectivity and higher Cyone selectivity comparing with other catalysts (Entries 3 and 5, Table 1). Cyone is an over-oxidation product of Cyol. Though the radical was also produced in the reaction using catalysts with HSO₄, NO₃, or BF₄ as anion, it is quite difficult to form an intermediate modified by HSO₄, NO₃, or BF₄ group (As far as we known, there is little compound forming covalent bond

DOI: 10.1039/C6GC02186G Journal Name

ARTICLE

with HSO_4 , NO_3 , or BF_4 group). Hence, the Cyone selectivity

Table 2 E conditior	Epoxidation of Is ^a	cyclohe	kene und	ler diffe	erent	
Entry	Colvent	T (***)	conv.	Selectivity (%)		
Entry	Intry Solvent I(C)		(%)	СНО	Cyol	Cyone
1	CH ₃ CN	20	6	90	2	5
2	CH₃CN	30	34	88	2	5
3	CH₃CN	40	55	85	2	6
4	CH₃CN	50	72	83	2	6
5	CH₃CN	60	99	82	2	11
6	CH ₃ CN	70	>99	71	2	18
7	THF	60	33	40	8	15
8	CH₃OH	60	3	76	7	16
9	CH_3COCH_3	50	6	44	5	19
10	CCI_4	60	74	<1	9	15
11	DMSO	60	2	74	1	3
12 ^b	CH₃CN	60	77	88	2	8
13 ^c	CH₃CN	60	11	88	7	5
14 ^d	CH₃CN	60	18	80	4	11
15 ^e	CH₃CN	60	5	42	5	54
16 ^f	CH₃CN	60	41	5	18	42
17 ^f	CH₃CN	60	85	63	5	17
18 ^f	CH₃CN	60	98	73	3	15
19 ^f	CH₃CN	60	>99	82	2	12

catalyst-to-substrate molar ratios is 1:1250, O₂ bubbling (1atm), reaction time: 10 hours; ^b2-Ethylbutyraldehyde as coreducant; ^c1-pentanecarbaldehyde as co-reducant; ^d1-Butalyde as co-reducant; ^e2-Furanaldehyde as co-reducant; ^tthe molar ratio of isobutyraldehyde to cyclohexene of Entries 16-19 are 0. 0.6. 0.8. 1.2. Products formed in the epoxidation reactions with olefins were identified by GC and GC-MS.

The effects of reaction temperature, Solvent and co-reductant

As shown in Table 2, the conversion of cyclohexene increased with the increasing of reaction temperature (Entries 1-6). Low temperature is favorable for the producing of CHO. As the temperature increases, the selectivity of over-oxidation product Cyone also increases.

The oxidation of cyclohexene is sensitive to solvent (Entry 5 and Entries 7-11). Being similar to most of the cyclohexene oxidation catalyzed by other catalysts^{14, 21, 55-58}, reaction using acetonitrile as solvent give the best conversion. Because no MeCONH₂ was detected in the catalytic epoxidation, the possibility of involvement acetonitrile as a co-reactant that through peroxyimidic as an oxygen donor was not recognized^{21, 59}. Possible that low coordinating ability and aprotic nature of acetonitrile play the key roles in improving the activity of the catalyst in acetonitrile^{14, 21, 60}. The catalyst almost does not work in methanol, acetone, and DMSO.

The direct reaction of dioxygen with singlet organic molecules is a spin-forbidden process, since the ground state of molecular oxygen is a triplet with two unpaired electrons having parallel spins⁶¹. Several aerobic reactions involving the combined use of dioxygen with reducing agents such as Zn

power⁶², $NaBH_4^{63}$, 2-propanol⁶⁴ and aldehyde^{4, 40, 65-68} have been reported. Co-oxidation of cyclohexene and aldehyde which is essential for the activation of molecular oxygen, leads to the formation of CHO (main product) and appropriate acid under the investigated conditions. Five kinds of aldehyde have been investigated in the epoxidation of cyclohexene (Entry 5 12-15). 2-ethylbutyraldehyde Entries and 1and pentanecarbaldehyde as co-reductant provide better selectivity of CHO than isobutyraldehyde. However, better conversion of cyclohexene could be obtained when isobutyraldehyde as co-reductant.

The molar ratio of isobutyraldehyde-to- cyclohexene plays a key role in the epoxidation of cyclohexene using molecular oxygen. In the absence of isobutyraldehyde, allylic oxidation is more favorable (Entry 16). Thus the epoxidation with various molar ratios of isobutyraldehyde-to-cyclohexene were examined. When the substrate-to-isobutyraldehyde molar ratio was increased from 0 to 1.0 (Entry 5 and Entries 16-18), the conversion of cyclohexene and the selectivity of CHO could be significantly increased, and the rate of epoxidation could be accelerated simultaneously. However, no significant difference was observed when the isobutyraldehyde/substrate molar ratio is increased to 1.2 (Entry 19).

Catalyst recycling experiment

The stability and recyclability of a catalyst is an important issue for its practical application⁵². The catalyst used here is ionic compound and its solubility in the reaction solvent is very poor. After the oxidation reaction catalyzed by [Cu-Imace-H-H][BF₄] finished, the catalyst can be simply filtrated and reused without any regeneration process. After six runs, there is no significant loss of the reactivity and selectivity (Fig. 3).



Fig. 3. Reuse of the catalyst in the oxidation of cyclohexene.

Radical inhibition reaction

Breen Chemistry Accepted Manuscript

Journal Name

It is widely accepted that the epoxidation of olefins in the liquid phase is a radical reaction^{21,69}. In order to verify whether the epoxidation reaction catalysed by [Cu-Imace-R-H] [X] was via radical intermediate or not, a radical inhibitor 3, 5-di-tert-butyl-p-hydroxytoluene (BHT) was added into the catalytic system. It was found that the epoxidation of cyclohexene reaction was quenched immediately after the adding of BHT

(see Fig. S1 in the ESI). The result indicates that radicals are involved in the catalytic cycle. The epoxidation of cyclohexene with dioxygen does not proceed without the presence of copper catalyst or without isobutyraldehyde (Fig. 1), which indicates that the chain reaction is initiated by the interaction between isobutyraldehyde and copper catalyst.

Table 3 Epoxidation of different olefins catalyzed by [Cu-Imace-H-H][BF ₄] ^a								
Entry	substrates	Loading (ppm)	Time (h)	Conv. (%)	TOF (h ⁻¹)	Main products and selectivity (%) ^c		
1	2a	1	8	99	123750	∽∽∽ ^C O ₉₇₍₉₂₎		
2		1	8	96	120000	<u>م</u> <u>98(87)</u>		
3	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1	8	91	113750	98		
4 ^d	∠] _{2d}	10	6	99	16500	98		
5	◯ _{2e}	10	8	93	11625	O 99		
6	2f	10	8	98	12250	10 ₉₆		
7	€ Let a let	1	10	93	93000	99		
8	OH ↓ 2h	10	12	89	7416	OH 96		
9	о 2i	100	12	63	525	97 97		
10	≻ → _{2j}	1	6	89	148333	Y 98		
11	Y O 2k	100	12	42	350			
12		100	12	53	442	55 A 45		
	21	800	10	76	95	54 46		
13	\sum	100	12	66	550			
	₩₩ 2m	800	10	92	115	69 J		
14		100	12	41	342			
	2n	800	10	70	88	55 5 ^{cl} 22		

DOI: 10.1039/C6GC02186G Journal Name

^a Reaction condition: substrate (0.2mol), isobutyraldehyde (0.2mol), CH₃CN (50mL), temperature: 60 $^{\circ}$ C, O₂ bubbling (1atm).^b TOF=(the initial moles of substrate × conversion)/(the moles of loading catalyst × reaction time). ^c The products were analyzed by GC and GC-MS. The yields were determined by GC using o-dichlorobenzene as internal standard. Values in parentheses are isolated yield. ^d Reaction temperature: 40 $^{\circ}$ C.

3.

5.

6.

7.

8.

9.

Epoxidation of various substrates catalyzed by [Cu-Imace-H-H][BF₄]

Under the optimized conditions, oxidation of various olefins were investigated (Table 3). The substrates include internal and terminal olefins, tri- and tetra-substituted olefins, and aromatic olefins. The catalyst is reactive for all the substrates investigated here. But the conversions and epoxides vields depend strongly on the olefin structures. The conversion of 2a-2g are larger than 90% using 1 or 10 ppm catalysts within 10 hours. For the oxidations of ketene (2i and 2k), only 63% and 42% conversions were achieved in 12 hours even when 100 ppm catalyst was used. Aromatic olefins seem to be relatively low activity, they need higher catalyst loading and longer reaction time for satisfied conversion. Comparing with styrene, 4-methylstyrene has a better conversion due to the electrondonating effect of methyl. Similarly, due to the electronwithdrawing effect, the conversion of 4-chlorostyrene only reached 70% with 10h.

The substrate investigated here can be divide into two different categories: aromatic and nonaromatic olefins. For the nonaromatic olefins (Entries 1-11, Table 3), the epoxide selectivity are high (>95%). For the aromatic olefins, the metal acetate compound can add to the C=C double bound and results in aromatic aldehydes under oxidation condition ⁷⁰. Besides, the radical intermediate generated by isobutyraldehyde and oxygen favours breaking of the olefins double bond²¹. Hence, a mixture of products were obtained for the aromatic olefins (Entries 12-14, Table 3).

Conclusions

We demonstrated that the copper catalyst with an imidazole salt tag ([Cu-Imace-R-H] [X], X'=F', Cl^{*}, Br', I', CF₃CO₂^{*}, HSO₄^{*}, NO₃^{*}, PF₆^{*}, or BF₄^{*}; R=H or CH₃) were efficient catalysts for the oxidation of olefins by dioxygen. Under mild temperature and atmospheric pressure, the catalytic system displays high reactivity by using ppm level of catalyst. The TOF of cyclohexene epoxidation reaction could reach up to 900000 h⁻¹. Moreover, the anion evidently affects the electronic structure of the catalysts, as well as their catalytic reactivity. In addition, the catalysts are relatively stable and can be reused at least six times with almost unchanged catalytic activity.

Molecular oxygen as oxidant, ppm level of cheap copper catalyst, mild reaction condition, good selectivity, and wonderful recyclability of the catalyst make these oxidation processes highly practical. It should be noted that the isobutyraldehyde used in the epoxidation reaction was stochiometrically transformed to isobutyric acid. To make the process more environmentally benign, isobutyraldehyde

should be recycled. There have many papers concerning the reduction of acid to aldehyde, which makes the reusing of isobutyraldehyde feasible^{71, 72}.

Acknowledgements

We gratefully acknowledge the grants from the National Natural Science Foundation of China (No.21476105, 21676134 and 21176110).

Notes and references

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China. Fax: +86 2583 336599; Tel: +86 2583 596665;

E-mail: huxb@nju.edu.cn; zbzhang@nju.edu.cn.

- M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang and T. Hyeon, Angew. Chem. Int. Ed., 2007, 46, 7039-7043.
- A. Fingerhut, O. V. Serdyuk and S. B. Tsogoeva, Green Chem., 2015, 17, 2042-2058.
 - Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu and K.-X. Su, *Chem. Rev.*, 2005, **105**, 1603-1662.
- Y. Qi, Y. Luan, J. Yu, X. Peng and G. Wang, *Chem. Eur. J.*, 2015, **21**, 1589-1597.
 - S. P. de Visser and S. Shaik, J. Am. Chem. Soc., 2003, **125**, 7413-7424.
 - W. Wu and H. Jiang, *Acc. Chem. Res.*, 2012, **45**, 1736-1748.
 - A. Wang, H. Jiang and H. Chen, J. Am. Chem. Soc., 2009, 131, 3846-3847.

D. Y. Kim, Y. J. Choi, H. Y. Park, C. U. Joung, K. O. Koh, J. Y. Mang and K.-Y. Jung, *Synth. Commun.*, 2003, **33**, 435-443.

- B. Bahramian, V. Mirkhani, M. Moghadam and S. Tangestaninejad, *Catal. Commun.*, 2006, 7, 289-296.
- B. Wang, Y. M. Lee, M. S. Seo and W. Nam, Angew. Chem. Int. Ed., 2015, 54, 11740-11744.
- 11. C. R. Turlington, D. P. Harrison, P. S. White, M. Brookhart and J. L. Templeton, *Inorg. Chem.*, 2013, **52**, 11351-11360.
- K. B. Sharpless and R. Michaelson, J. Am. Chem. Soc., 1973, 95, 6136-6137.
- D. Banerjee, R. V. Jagadeesh, K. Junge, M. M. Pohl, J. Radnik, A. Brückner and M. Beller, *Angew. Chem. Int. Ed.*, 2014, 53, 4359-4363.
- 14. Z. Chen and R. L. Luck, *Green Chem.*, 2016, **18**, 3354-3359.
- 15. C. Wang and H. Yamamoto, J. Am. Chem. Soc., 2014, **136**, 1222-1225.
- M.-D. Zhou, M.-J. Liu, L.-L. Huang, J. Zhang, J.-Y. Wang, X.-B. Li, F. E. Kühn and S.-L. Zang, *Green Chem.*, 2015, **17**, 1186-1193.
- S. Doherty, J. G. Knight, J. R. Ellison, D. Weekes, R. W. Harrington, C. Hardacre and H. Manyar, *Green Chem.*, 2012, 14, 925-929.
 - M. Jafarpour, A. Rezaeifard, M. Ghahramaninezhad and F. Feizpour, *Green Chem.*, 2015, **17**, 442-452.

18.

54.

55.

56.

58.

63.

64.

68.

- G. Chatel, C. Goux-Henry, N. Kardos, J. Suptil, B. 19. 49. Andrioletti and M. Draye, Ultrason. Sonochem., 2012, 19, 390-394 50.
- 20. L. Ji, Y.-N. Wang, C. Qian and X.-Z. Chen, Synth. Commun., 2013, 43, 2256-2264.
- 21. L. Hadian-Dehkordi and H. Hosseini-Monfared, Green Chem., 2016, 18, 497-507.
- 22. F. Montanari and L. Casella, Metalloporphyrins catalyzed oxidations, Springer Science & Business Media, 2013.
- 23. S. Nakagaki, K. M. Mantovani, G. Sippel Machado, K. A. Dias de Freitas Castro and F. Wypych, Molecules, 2016, **21**. 291.
- 24. K. Zhang, O. K. Farha, J. T. Hupp and S. T. Nguyen, ACS Catalysis, 2015, 5, 4859-4866.
- 25. T.-S. Lai, S. K. Lee, L.-L. Yeung, H.-Y. Liu, I. D. Williams and C. K. Chang, Chem. Commun., 2003, 620-621.
- 26. J.-L. Zhang and C.-M. Che, Org. Lett., 2002, 4, 1911-1914.
- J. Chen and C. M. Che, Angew. Chem. Int. Ed., 2004, 43, 27. 4950-4954.
- 28. R. De Paula, M. M. Simões, M. G. P. Neves and J. A. Cavaleiro, Catal. Commun., 2008, 10, 57-60.
- J. Lu, L. Liang and M. Weck, J. Mol. Catal. A: Chem., 2016, 29. 417. 122-125.
- 30. P. Fackler, S. M. Huber and T. Bach, J. Am. Chem. Soc., 2012, 134, 12869-12878.
- 31. J. W. Brown, Q. T. Nguyen, T. Otto, N. N. Jarenwattananon, S. Glöggler and L.-S. Bouchard, Catal. Commun., 2015, 59, 50-54.
- 32. W. Nam, S.-E. Park, I. K. Lim, M. H. Lim, J. Hong and J. Kim, J. Am. Chem. Soc., 2003, 125, 14674-14675.
- 33. S. Funyu, T. Isobe, S. Takagi, D. A. Tryk and H. Inoue, J. Am. Chem. Soc., 2003, 125, 5734-5740.
- 34. E. T. Saka, D. Çakır, Z. Bıyıklıoğlu and H. Kantekin, Dyes and Pigments, 2013, 98, 255-262.
- E. Angelescu, R. Ionescu, O. Pavel, R. Zăvoianu, R. Birjega, 35. C. Luculescu, M. Florea and R. Olar, J. Mol. Catal. A: Chem., 2010, 315, 178-186.
- 36. E. M. McGarrigle and D. G. Gilheany, Chem. Rev., 2005, 105. 1563-1602.
- 37. C. J. Chang, J. A. Labinger and H. B. Gray, Inorg. Chem., 1997, **36**, 5927-5930.
- 38. X. Yun, X. Hu, Z. Jin, J. Hu, C. Yan, J. Yao and H. Li, J. Mol. Catal. A: Chem., 2010, 327, 25-31.
- 39. K. Srinivasan, P. Michaud and J. K. Kochi, J. Am. Chem. Soc., 1986, 108, 2309-2320.
- W. Zhang, J. L. Loebach, S. R. Wilson and E. N. Jacobsen, J. 40. Am. Chem. Soc., 1990, 112, 2801-2803.
- 41. T. Punniyamurthy, S. Velusamy and J. Igbal, Chem. Rev., 2005, 105, 2329-2364.
- Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan and J. Suo, 42. J. Mol. Catal. A: Chem., 2004, 218, 161-170.
- 43. O. A. Wong and Y. Shi, Chem. Rev., 2008, 108, 3958-3987.
- Q. Zhao, C. Bai, W. Zhang, Y. Li, G. Zhang, F. Zhang and X. 44. Fan, Ind. Eng. Chem. Res., 2014, 53, 4232-4238.
- 45. H. Srour, P. Le Maux, S. Chevance and G. Simonneaux, Coord. Chem. Rev., 2013, 257, 3030-3050.
- X.-T. Zhou, H.-B. Ji, J.-C. Xu, L.-X. Pei, L.-F. Wang and X.-D. 46. Yao, Tetrahedron Lett., 2007, 48, 2691-2695.
- 47. N. A. Stephenson and A. T. Bell, J. Mol. Catal. A: Chem., 2006, 258, 231-235.
- 48. X. Hu, Y. Sun, J. Mao and H. Li, J. Catal., 2010, 272, 320-332.

- G. Yang, X. Hu, Y. Wu, C. Liu and Z. Zhang, Catal. Commun., 2012, 26, 132-135.
- X. Hu, C. Liu, Y. Wu and Z. Zhang, The Journal of Physical Chemistry C, 2011, 115, 23913-23921.
- L. Yuan, Y. Xu, X. Hu, G. Yang and Y. Wu, J. Mol. Catal. A: 51. Chem., 2015, 396, 55-60.
- 52. Y. Cao, H. Yu, F. Peng and H. Wang, ACS Catalysis, 2014, 4, 1617-1625.
- X. He, L. Chen, X. Zhou and H. Ji, Catal. Commun., 2016, 53. 83. 78-81.
 - A. E. Wendlandt, A. M. Suess and S. S. Stahl, Angew. Chem. Int. Ed., 2011, 50, 11062-11087.
 - Y. Xu, A. Li, X. Jia and Z. Li, Green Chem., 2011, 13, 2452-2458
 - A. Farokhi and H. Hosseini-Monfared, New J. Chem., 2016, 40. 5032-5043.
- R. A. Moretti, J. Du Bois and T. D. P. Stack, Org. Lett., 57. 2016, 18, 2528-2531.
 - E. Tebandeke, C. Coman, K. Guillois, G. Canning, E. Ataman, J. Knudsen, L. R. Wallenberg, H. Ssekaalo, J. Schnadt and O. F. Wendt, Green Chem., 2014, 16, 1586-1593.
- 59. G. B. Payne, P. H. Deming and P. H. Williams, J. Org. Chem., 1961, 26, 659-663.
- 60. M. Guidotti, C. Pirovano, N. Ravasio, B. Lazaro, J. M. Fraile, J. A. Mayoral, B. Coq and A. Galarneau, Green Chem., 2009, 11, 1421-1427.
- D. H. Barton, A. E. Martell and D. T. Sawyer, The activation 61. of dioxygen and homogeneous catalytic oxidation, Springer Science & Business Media, 2012. 62.
 - Y. Moro-oka, Catal. Today, 1998, 45, 3-12.
 - B. Johnson and M. Twigg, Transition Met. Chem., 1985, 10. 439-440.
 - T. Mukaiyama and T. Yamada, Bull. Chem. Soc. Jpn., 1995, 68, 17-35.
- 65. J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek and S. A. Raybuck, J. Am. Chem. Soc., 1985, 107, 2000-2005.
- E. Tebandeke, C. Coman, K. Guillois, G. Canning, E. 66. Ataman, J. Knudsen, L. R. Wallenberg, H. Ssekaalo, J. Schnadt and O. F. Wendt, Green Chem., 2014, 16, 1586-1593.
- S. Koya, Y. Nishioka, H. Mizoguchi, T. Uchida and T. 67. Katsuki, Angew. Chem. Int. Ed., 2012, 51, 8243-8246.
 - A. Rezaeifard, R. Haddad, M. Jafarpour and M. Hakimi, J. Am. Chem. Soc., 2013, 135, 10036-10039.
- A. Appelton, S. Evans and J. L. Smith, J. Chem. Soc. Perkin 69. Trans, 1996, 2, 281-285.
- 70. B. Feng, Z. S. Hou, X. Wang, Y. Hu, H. Li and Y. Qiao, Green. Chem., 2009, 11, 1446-1452.
- K. Nagayama, I. Shimizu and A. Yamamoto, Chem. Lett., 71. 1998, 11, 1143-1144.
- J. S. Cha, J. H. Park and D. Y. Lee, Bull. Korean Chem. Soc. 72. 2001, 22, 325-326.

Table of contents entry:



 O_2 as oxidant, ppm catalyst loading, mild reaction condition, good selectivity, and wonderful recyclability of the catalyst for the oxidation of olefins.