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Binuclear molybdenum Schiff-base complex: An efficient catalyst for the epoxidation of alkenes



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Keywords: Dimolybdenum complex Olefin epoxidation catalyst Binuclear Schiff-base Recyclable catalyst	Dimolybdenum Schiff-base complex (DMSBC) which contain O, <i>N</i> -bidentate ligand was synthesized and char- acterized. The complex can be used as a promising catalyst in the epoxidation of olefins with tert-butyl-hy- droperoxide (TBHP) as oxidant. The catalytic activity of the DMSBC was optimized by adjusting various para- meters. Epoxidation of olefins by DMSBC indicated that the catalyst exhibited superb catalytic activity with high conversions up to 99.6%, high selectivity up to 100%, and high turnover frequency (TOF) of $208 h^{-1}$. Kinetic analysis provided that epoxidation of cyclooctene by DMSBC possessed moderate activation energy (95.3 \pm 2 kJ·mol ⁻¹). Furthermore, the calculated pre-exponential factor (<i>A</i>) proved that strong collisions probability take place in the reaction. Additionally, the recycle experiments demonstrated that DMSBC could be recovered and repeatedly applied

1. Introduction

Epoxide is one of the worthiest chemical intermediates for producing various important industrial products, such as surfactants, epoxy resins, lubricating oils, textiles, cosmetics, surface coatings, corrosion protection agents, pesticides, detergents, sweeteners, chiral pharmaceuticals, perfumes, and so on [1,2]. One of the most efficient method to produce epoxides is the epoxidation of alkenes. Epoxides were obtained with high yields and high selectivity by the assistant of heterogeneous/homogeneous catalysts or stoichiometric amounts of per-acids [3–6]. However, per-acids can induce environmental pollution and require high cost. In order to shrink the extravagant use of large amounts of oxidants, such as per-acids and sodium hypochlorite, the catalysts based on transition metal have been extensively developed [7–12].

As a sustainable world development, the awareness of environmental protection is increasing. The use of nontoxic, and resource-rich metals, such as molybdenum, has attracted more and more attentions. In the industry, promising economic effect has been obtained by the production of propylene oxide with molybdenum as well as alkyl hydroperoxides as oxidants (named Halcon-Arco process) [13]. Furthermore, various kinds of molybdenum-base catalysts have been developed as heterogeneous catalysts in epoxidation reaction. One typical example is the usage of $[Mo(CO)_6]$ and alkyl peroxide [14-18]. Besides, the catalyst consisted of molybdenum and various kinds of ligands has been used for the epoxidation of olefins and presented excellent catalytic activity with high yields and high selectivity [19]. It is noteworthy that the complexes consisted of Schiff-base ligands and molybdenum are highly efficient homogeneous/heterogeneous catalysts [20-24]. Recently, the epoxidation of terminal olefins are accomplished by molybdenum Schiff-base complexes. According to previous works, most molybdenum Schiff-base complexes are efficient homogeneous catalysts. Generally, homogeneous catalysts could be used under mild reaction conditions [25-27]. However, the drawbacks of homogeneous catalyst, including unrecyclable ability and poor stability, urgently need to be solved. Heterogeneous catalysts are gained much attention compared to homogeneous catalysts since they could be easily separated and recycled from reaction mixture, which makes them play a critical role in the development of environmentally friendly and sustainable processes [28-31]. Mahdi Mirzaee al. used boehmite nanoparticles (BNPs) anchor Schiff base to generate molybdenum complexes, which could transform unreacted cis-cyclooctene to epoxy cyclooctane with good catalytic performance [32]. Maryam Zare al. immobilized molybdenum (VI) complex onto Fe₃O₄/SiO₂ as heterogeneous catalyst, and had realized the catalyst recycle from the mixture [33]. Behnam Babaei al. had prepared the catalyst by tethering a molybdenum (VI) Schiff-base complex via post-synthesis modification of MnFe₂O₄ nanoparticles and the catalyst was recycled and reused several times [34]. Nevertheless, those methods may lead to the loss of

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catalyst activity. Therefore, it is eagerly desirable but still highly challenging to develop novel heterogeneous catalysts with high catalytic efficiency.

In this work, a novel dimolybdenum Schiff-base complex (DMSBC) was obtained by the reaction of $MoO_2(acac)_2$ and a binuclear Schiffbase ligand (H₂L). The DMSBC acted as heterogeneous catalyst in the epoxidation of some cyclic and terminal olefins. The result revealed that DMSBC exhibited excellent catalytic efficiency in the epoxidation of various linear and cyclic alkenes. Moreover, the kinetic analysis of catalytic oxidation was investigated to determine the activation energy of catalyst. Besides, DMSBC exhibited poor solubility at ambient temperature in some organic solvents. In addition, it could be separated from the reaction mixture mainly by filtration and centrifugation, and successfully reutilized at least three times without significantly reducing the catalytic efficiency, and could be use six times still have the catalytic efficiency.

2. Materials and methods

2.1. Synthesis materials

All commercial grade solvents and chemical reagents were purchased and used without further purification. Infrared spectra of solid samples were recorded with a Nicolet iS50 fourier transform infrared (FT-IR)spectrometer in the range of $4000-400 \text{ cm}^{-1}$ using KBr-disk method. ¹H NMR spectra were observed on a Bruker Avance III (500 MHz). The mass spectra were performed on Agilent LC-QTOF mass spectrometer. Gas chromatography (GC) measurements were carried out on a ShimadzuGC-2010 gas chromatograph. Elemental analysis was performed on Vario EL cube. The X-ray photoelectron spectroscopy was performed on ESCALAB 250.

2.2. Synthesis of O,N-bidentate Schiff-base ligand (H₂L)

A typical process for the synthesis of symmetrical Schiff-base ligand by the condensation of the amino group with the aldehyde group was described (Scheme 1a) [35]. A mixture of 4-(diethylamino)salicylaldehyde (6 mmol) and MeOH (25 mL) was added drop-wise into a



Scheme 1. Procedure for the synthesis of a: binuclear salophen ligand and b dimolybdenum Schiff-base complex (DMSBC).

mixture of 3,3-diaminobenzidine (1 mmol) and MeOH (25 mL) under continuous stirring at 80 °C, and then the brown mixture was refluxed for 24 h until a deep orange to red mixture was obtained. The rude product was collected by centrifugal separation. Subsequently, the orange product was obtained and recrystallized from MeOH for several times, then the product was collected by centrifugal separation and dried (Yield:87%). ¹HNMR (500 MHz, CDCl₃, TMS) = 1.23 (t, 24H, CH₃), 3.44 (m, 16H, CH₂), 6.26 (t, 8H, CH), 7.02 (m, 4H, CH), 7.07 (d, 2H, CH), 7.22 (t, 4H, CH), 8.50 (s, 4H, CH), 13.48 (s, 4H, OH). ¹³C NMR (151 MHz, CDCl₃) δ 164.70 (d, J = 16.9 Hz), 160.96 (s), 160.26 (s), 151.98 (d, J = 10.4 Hz), 142.02 (d, J = 133.0 Hz), 138.31 (s), 133.98 (d, J = 27.7 Hz), 124.42 (s), 119.34 (s), 117.49 (s), 109.61 (d, J =7.5 Hz), 103.76 (s), 98.22 (s), 44.59 (s), 12.78 (s). MS(ESI): m/ $z = 915.528 [M+H]^+$. $C_{56}H_{66}N_8O_4$ (914.52): calcd. Anal calcd for C₅₆H₆₆N₈O₄: C, 73.49; H, 7.27; N, 12.24. Found: C, 73.35; H, 7.28; N, 12.26.

2.3. Synthesis of symmetrical dimolybdenum Schiff-base complex (DMSBC)

MoO₂(acac)₂ (2.2 mmol) and binuclear Schiff-base ligand (H₂L) (2 mmol) were mixed in MeOH (80 mL) under nitrogen atmosphere (Scheme 1b). The solution rapidly turned to crimson and then was stirred at 80 °C for 24 h. The MeOH was evaporated under vacuum and crimson solid was obtained. The crimson solid was collected by centrifugal separation and washed by MeOH for several times. The crimson solid was obtained after dried in vacuum (Yield:82%). ¹H NMR (500 MHz, DMSO, TMS) = 1.10 (t, 12H, CH₃), 3.42 (m, 8H, CH₂), 6.04 (s, 2H, CH), 6.37 (d, 2H, CH), 6.84 (d, 1H, CH), 7.43 (t, 4H, CH), 8.81 (d,1H, CH), 9.22 (d, 1H, CH). ¹³C NMR (151 MHz, DMSO) δ 165.47-165.08 (m), 164.33 (s), 163.87 (s), 154.16 (d, *J* = 34.2 Hz), 152.14 (s), 136.92-136.65 (m), 134.54-134.26 (m), 115.12-114.69 (m), 112.23 (s), 111.68 (s), 99.36 (s), 97.39 (s), 96.38 (s), 44.55 (t, J = 17.7 Hz), 19.04 (s). Anal Calcd for C₅₆H₆₂Mo₂N₈O₈: C, 57.63; H, 5.35; N, 9.60. Found: C, 57.21; H, 5.23; N, 9.48.

2.4. General procedure for the epoxidation of alkenes

In a typical procedure, a mixture of catalyst (50 mg 0.04 mmol), substrate (10 mmol), 1,2-dichloroethane (10 ml) and TBHP (30 mmol) (Table 2) was stirred and heated to the appropriate temperature in oil bath for pre-determined time. At the end of the reaction, the catalyst was removed by centrifugation and the product was analyzed by gas chromatography.

3. Results and discussion

3.1. The characterizations of free H_2L and DMSBC

Fourier-transform infrared (FT-IR) spectroscopy curves of five samples were shown in Fig. 1. The characteristic C–O stretching vibrations and C–N asymmetric stretching vibrations could be found in the range of 1236 cm^{-1} and 1330 cm^{-1} . A meaningful characteristic band at 1620 cm^{-1} belonged to the vibration of C—N group, which proved the successful reaction of imines groups with aldehydegroups (Schiff base) [32]. As shown in Fig. 1d, a new peak at 904 cm^{-1} was assigned to Mo = O stretching vibration of DMSBC comparing to Fig. 1c, which may due to coordination of molybdenum to Schiff-base ligand [36,37].

3.2. The X-ray photoelectron spectroscopy (XPS) of DMSBC

The XPS spectrum of DMSBC is shown in Fig. 2. From the XPS survey spectrum (Fig. 2a), bands at 232.4 eV (Mo3d), 285 eV (C1s), 400.5 (N1s), 410 eV (Mo3p), and 529 (O1s) could be used to determine the chemical composition of catalyst. The Mo3d core level spectrum (Fig. 2b) shows the dominant Mo3d3/2 and Mo3d5/2 peaks at 232.6 eV



Fig. 1. FT-IR spectra of (a) 4-(Diethylamino)salicylaldehyde (b) 3,3-Diaminobenzidine (c) Binuclear Schiff-base ligand (H_2L) (d) Fresh catalyst (DMSBC) (e) Used catalyst (DMSBC) after six runs.

and 235.7 eV, which indicated that the Mo species are retained in the +6 oxidation state in DMSBC. The major role of the molybdenum (VI) ion is to withdraw electrons from the peroxidic-oxygens, making them more susceptible to attack by nucleophiles such as olefins. The O1s core level spectrum (Fig. 2c) could be deconvoluted into two bands: 530.79 for oxo-oxygen, and 532.17 for peroxo-oxygen respectively.

3.3. Study of the catalytic activity of DMSBC in the epoxidation of cyclooctene

The action scheme of the catalyst in the epoxidation of cyclooctene



Scheme 2. Epoxidation of cyclooctene with DMSBC.

was illustrated in Scheme 2. The result (Fig. 3) described 92.0% conversion and almost 100% selectivity within 1 h, revealing the catalyst has high catalytic activity.

3.3.1. The influence of solvent on catalytic activity of DMSBC

The catalytic activity of DMSBC was investigated in non-polar, polar aprotic, polar protic solvents and the solvents ordered by increasing polarity. The highest activity of DMSBC was obtained in 1,2-dichloroethane ($C_2H_4Cl_2$) (Table 1), which could be explained by the theory of hard and soft acid base (HSAB) [36]. Coordinating solvents such as acetonitrile (CH₃CN), dimethylformamide (DMF) and ethanol (EtOH) may compete with tert-butyl hydroperoxide (TBHP) to occupy the coordination sites on the hard Mo(VI) ion, leading to the remarkable reduction of the conversion. On the other side, the higher conversion and selectivity were obtained in the non-coordinative solvents such as 1,2-dichloroethane ($C_2H_4Cl_2$) and chloroform (CHCl₃), which may be attributed to the coordination of TBHP to Mo (VI) center followed by transfer of oxygen to alkenes [35].

3.3.2. Proposed mechanism of the epoxidation of cyclooctene in the presence of DMSBC

Although the mechanism of epoxidation of olefin is still controversial, the mechanism about the coordination of TBHP to Mo (VI) center resulted in the formation of MoO-H and MoO₂-tBu moieties, which was more possible [32,36,38]. The mechanism is shown in



Fig. 2. XPS survey spectra of (a) DMSBC (b) Core level spectra of Mo3d,and (c) Core level spectra of O1s.



Fig. 3. The catalytic activity of DMSBC in the epoxidation of cyclooctene.

Reaction conditions: catalyst (50 mg 0.04 mmol), cyclooctene (10 mmol), C₂H₄Cl₂ (10 ml), TBHP(30 mmol) and 80°C reflux. Selectivity and yields were determined by GC, Selectivity toward the corresponding epoxide.

Table 1

The influence of solvent on catalytic activity of DMSBC (cyclooctene as substrate)^a.

Entry	Cat.(mg)	solvent	T(°C)	Time(h)	Conversion (%)	Selectivity (%)
1	50	DMF	80	12	7.0	94.4
2	50	CH_3CN	80	12	44.5	93.5
3	50	EtOH	80	12	64.3	93.0
4	50	CHCl ₃	80	12	75.6	94.8
5	50	$C_2H_4Cl_2$	80	1	92.0	99.6

^a Reaction conditions: catalyst (50 mg 0.04 mmol), cyclooctene (10 mmol), solvent (10 ml), TBHP(30 mmol) and reflux. Selectivity and yields were determined by GC, Selectivity toward the corresponding epoxide.

Table 2

The result of the epodxidation of cyclooctene by DMSBC with different amount of ${\rm TBHP^{a}}.$

Entry	Cat.(mg)	solvent	TBHP (mM)	Conversion (%)	Selectivity (%)
1	50	$C_2H_4Cl_2$	10	37.9	77.4
2	50	$C_2H_4Cl_2$	20	71.7	77.4
3	50	$C_2H_4Cl_2$	30	92.0	99.6

 $^{\rm a}$ Reaction conditions: catalyst (50 mg 0.04 mmol), 10 mmol cyclooctene, 1,2-dichloroethane (10 ml), time (1 h) and reflux. Selectivity and yields were determined by GC, Selectivity toward the corresponding epoxide.



Scheme 3. Proposed mechanism of the epoxidation of cyclooctene in the presence of DMSBC and TBHP.

Table 3

Epoxidation of different alkenes in the r	presence of DMSBC
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Entry	Cat. (mg)	Time (h)	Alkenes	T (°C)	Conversion (%)	Selectivity (%)	TOF
1	none	10	cyclooctene	80	3.9	85.0	
2	50	12	styrene	80	49.9	4.6	7.4
3	50	1	cyclooctene	80	92.0(99.*) ^a	99.6	208
4	50	12	octylene	80	63.9	100	7.0
5	50	5	cyclohexene	80	91.0(99.*) ^b	100	33.0
6	50	12	hexene	80	90.0	100	6.3
7	50	10	Norbornene	80	98.1	90.4	29.0

Complete conversion after $3 h_1 > 99\%$.

^b Complete conversion after 4 h, > 99%.



Fig. 4. (a) The conversion profiles of cyclooctene obtained at the indicated reaction temperature by using DMSBC. (b) Arrhenius plot of the epoxidation of cyclooctene with DMSBC and TBHP.



Fig. 5. Catalyst reusability in the epoxidation of cyclooctene with TBHP and DMSBC.

Reaction conditions: cyclooctene (10 mmol), TBHP (30 mmol), 1,2-dichloroethane (10 ml) refluxing 1 h. Selectivity and yields were determined by GC, Selectivity toward the corresponding epoxide

Scheme 3. The progress of reaction has been monitored by electronic absorption spectroscopy (Fig S6, Supporting Information). A absorption band observed at 230 nm is probably due to n to π transition of the -C = N- and -C = O- of the ligand. The spectra of DMSBC sho wa band at 410 nm, which assign to the ligand to metal(molybdenum atom) charge transfer (LMCT) [39–42]. The addition of TBHP causes the decrease in intensities of the 410 band. The change along with the generation of an isosbestic point at 410 nm indicate the interaction of catalyst with TBHP and the plausible formation of the corresponding peroxido complex. Although the isolation of the real intermediates has not been successfully achieved, the formation of relevant dioxidomolybdenum (VI) complexes with TBHP to generate $[Mo(VI)O(O_2)]^{2+}$ complexes has been reported [43,44]. However, the addition of cyclooctene into the above solution does not obviously change the wavelengths of observable absorption peaks. Based on the obtained oxidation products and experiments described above, a reaction pathway including oxido-peroxido intermediates can be rationally proposed. The catalyst is responsible for receiving and transferring oxygen atoms. Firstly, the TBHP proton transfer oxy-complex resulting in the coordination of TBHP to the molybdenum center. The α -O atom was then transferred to the olefin to produce the epoxide (the major product)

Table 4						
Catalytic activity of	various	catalysts	for	the epoxidation	of	cycl

Entry	Catalyst	Substrate	Solvent	Time (h)	Conv. (%)	TOF (h^{-1})	References
1	[MoO ₂ L]	Cyclooctene	$C_2H_4Cl_2$	1	92.0 (99.* ^a	208	This work
2	[MoO ₂ (Sal-Tryp)]	Cyclooctene	CCl_4	8	100	30.5	[36]
3	MoO ₂ (acac) ₂ @ UiO-66-NH ₂ -SA	Cyclooctene	$C_2H_4Cl_2$	0.75	97.0	61.0	[37]
4	MoO ₂ (acac) ₂ @ UiO-66-NH ₂ -TC	Cyclooctene	$C_2H_4Cl_2$	1	94.0	39.2	[37]
5	Mo-Im-BNPs	Cyclooctene	CCl_4	1	97.0	126	[31]
6	Mo-A-BNPs	Cyclooctene	CCl ₄	3.5	97.0	89.0	[31]

Complete conversion after 3 h, > 99%.

meanwhile releasing tert-butylalcohol (byproduct), yielding the initial catalyst. The mechanism could interpret the high reaction speed of electron-rich alkenes compared with electron-poor alkenes. Besides, this mechanism suggest the addition of TBHP increase the conversion of olefin, which agrees to our experiment results (Tables 2 and 3). Theoretical studies proved that the formation of hydrogen bond was extremely important during the reaction. Thus, not only the transfer of oxygen, but also the transfer of hydrogen has the barrier. The production of epoxy compounds has almost no barrier. In contrast, there is an obvious energy barrier on the release of tert-butylalcohol (Table 2) [38].

3.3.3. Epoxidation of alkenes with DMSBC

The DMSBC could also be used for the epoxidation of a wide range of alkenes. The control experiment shown that the yields still extremely low after ten hours reflux without catalyst (Table 3, Entry 1). On the contrary, some cyclic and terminal olefins could be effectively and selectively converted to epoxies in the presence of catalyst, which revealed the catalyst has good catalytic activity. In the epoxidation of endocyclic alkenes, the selectivity of epoxy compounds is almost 100%, which is due to the high activity of the double bonds and the relative high stability of epoxy products. Linear aliphatic olefins such as 1hexene and 1-octene converted to their corresponding 1,2-epoxy alkanes as an exclusive product. However, the conversion of 1-hexene (90.0%) was higher than 1-octene (63.9%) which suggested that catalytic activity decreases along with chain length of olefins. Larger hexyl group of 1-octene connected to double bond sterically hinders its approach to the active site compared to 1-hexene whose double bond carries a smaller butyl group. Due to the conjugative effect of benzene ring, styrene showed lower activity. Basing on the mechanism suggested above, higher electron donating olefins that have inner double bonds shows splendid activity comparing to terminal olefins. The product of the epoxidation reaction were collected at different time intervals and then identified and quantified by gas chromatography. The turnover frequency (TOF) was calculated as follows:

 $TOF = \frac{moles converted}{moles of Mo(active site) taken for reaction \times reaction time}$

3.3.4. Dynamics of the epoxidation of cyclooctene by DMSBC

To explore the source and activity of the catalyst for aerobic oxidation of olefins to form epoxy compounds, it is necessary to carry out kinetic analysis. In this present work, some key kinetic parameters were studied by using the oxidation of cyclooctene as a model reaction. Firstly, the effect of temperature on catalytic activity of catalyst was investigated [45]. Considering the selectivity of the reaction, we performed the reaction 323 K, 333 K, 343 K and 353 K (Fig. 4). As the result shown in Fig. 4, the conversion of cyclooctene increased gradually from 30.8% to 99.2% along with the reaction temperature increase from 323 K to 353 K. The reaction was carried out at different temperatures, and the initial k was obtained by the linear fitting of the time versus conversion curve. According to the Arrhenius equation of $\ln k = \ln k$ $A - E_a/RT$, we plotted the relationship between ln k and 1/T, which has excellent linear relationship (Fig. 4B $R^2 = 1$). Activation energy (E_a) and pre-exponential factors (A) obtained by the Arrhenius equation were 95.3 \pm 2 kJ·mol⁻¹ and 7.9 \times 10¹⁰ mol⁻¹ dm³·s⁻¹, respectively. The result indicated that the epoxidation of cyclooctene has high conversion speed and high probability of collision.

3.4. Recycling experiments of DMSBC for epoxidation of cyclooctene under optimized conditions

The stability and reusability both are the important properties for the preparation of heterogeneous catalyst. Fig. 5 indicated the results of epoxidation of cyclooctene. After each test, the DMSBC was simply separated by centrifugal, then washed, dried, and reused in the next

operation. The catalyst prepared in the epoxidation reaction of cyclooctene gained high conversion rate after 60 min of the first three runs. The catalytic activity of the catalyst in the fourth to sixth run showed suitable catalytic performance, but lower than the former three runs. One conclusion could be drawn is that the DMSBC was recycled used for the epoxidation of cyclooctene for three times without significantly reducing the catalytic efficiency. On the other hand, very low molybdenum species was detected in the filtrate for former two runs, which was confirmed by ICP analysis (Fig S7, Supporting Information). Moreover, no significant new peak can be found in FT-IR curve (Fig. 1e) when compared to that of fresh catalyst (Fig. 1d), proving the catalyst exhibited excellent stability. Small changes in signal intensity and position were probably due to overlapping or shifting of the band when tert-BuOH, and cyclooctene oxide coexisted [37]. Therefore, these stretching vibrations strongly confirm the retrievability and the stability of the catalyst.

3.5. Comparison with other catalysts

Asgharpour *al.* testified that the [MoO₂(Sal-Tryp)] catalyst could be used for the epoxidation of cyclooctene. They performed the reaction in CCl₄ and obtained 100% yield (Table 4, entry 2) [46]. Additional, Kardanpour et *al.* performed the epoxidation of cyclooctene by MoO₂(acac)₂@UiO-66-NH₂-SA and MoO₂(acac)₂@UiO-66-NH₂-TC in C₂H₄Cl₂ (Table 4, entry 3,4), which showed that those catalysts have good catalytic performances for epoxidation of alkenes [47]. Furthermore, Mirzaee et *al.* reported that Mo-Im-BNPs and Mo-A-BNPs could be reused several times without significant loss of activity and selectivity (Table 4, entry 5,6) [36]. In this work, 92.0% conversion and high turnover frequency is 208 h⁻¹ (Table 4, entries 1). Comparing with the reported catalysts (Table 4), this catalyst exhibited better catalytic property for epoxidation of turnover frequency.

4. Conclusion

A heterogeneous dimolybdenum Schiff-base catalyst was successfully prepared. The catalyst showed remarkable catalytic activity in the epoxidation of cyclic and terminal olefins. Based on the experiments, the results indicated that solvent strongly effect the reaction speed, selectivity and conversion on the epoxidation of olefins. Moreover, the highest yield (99%) and selectivity (99.6%) were obtained in 1,2-dichloroethane (C₂H₄Cl₂). Kinetic analysis indicated that dimolybdenum catalyst had moderate activation energy (95.3 \pm 2 kJ·mol⁻¹ for cyclooctene oxidation). The large pre-exponential factor (A) meant that there was a high probability of collision to account for the high reaction rate. Furthermore, the catalyst could be easily recovered by centrifugal. It could be reused at least six times with suitable catalytic performance.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110498.

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