A stable and highly selective metalloporphyrin based framework for catalytic oxidation of cyclohexene

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-04-2020-001420.R1
Article Type:	Paper
Date Submitted by the Author:	09-Jul-2020
Complete List of Authors:	Xia, Zhinan; Northeast Normal University Li, Fengyan; northeast normal university, Xu, Lin; Northeast Normal University, Department of Chemistry Feng, Pingyun; University of California, Department of Chemistry

ARTICLE

A stable and highly selective metalloporphyrin based framework for catalytic oxidation of cyclohexene†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Zhinan Xia,[a] Fengyan Li,*[a, b] Lin Xu,[a] and Pingyun Feng*[b]

A new metalloporphyrin framework of molybdenum $Mo_2O_4(C_{48}H_{28}N_4O_8)\cdot(CH_3)_2NH\cdot5H_2O\cdot2DMF$ (Mo_2TCPP) was synthesized from tetrakis(4-carboxyphenyl)porphyrin (H_4TCPP) and sodium molybdate dihydrate by hydrothermal method. Mo_2TCPP is a 3D network with two sub-units, in which both TCPP ligands and each Mo_2 dimer act as four connection nodes. The crystal structure was determined by single crysyal analysis and further characterized by FTIR, SEM, EDX, PXRD, XPS and TGA. Here cumene hydrogen peroxide and hydrogen peroxide were used as oxidants to study the catalytic activity of new metalloporphyrins to the oxidation of cyclohexene at different temperatures. The conversion rate of cyclohexene and the selectivity of epoxy cyclohexane were both higher than 99%, which was better than the previous published research results. The stability of the catalyst before and after the reaction was further tested for 10 runs without obvious degradation. The catalyst was stable in different solutions such as acidic, water and alkaline solutions. These results shed light on future development of the new catalytic materials based on metalloporphyrin.

Introduction

Metalloporphyrin molecules have been widely studied because of their many excellent properties in the last two decades.[1] The tetrakis (4-carboxyphenyl)porphyrin (H_4TCPP) is the most widely used porphyrin-based ligand in metal-metalloporphyrin frameworks. The first H_4TCPP-based material, $[CoT(p\text{-}CO_2)PPCo_{1.5}(C_5H_5N)_3(H_2O)]\cdot11C_5H_5N$ (PIZA-1), was reported in 2002. The selective adsorption of PIZA-1 to guest solvent molecules was reported.[2] Since then, dozens of materials synthesized from the same ligand have been reported including three-dimensional topologies.[3-12] These materials exhibited unique chemical, physical, and electronic structures and properties and played a number of important roles in molecular binding, reaction catalysis, energy and electron transfer, and light harvesting.[13-16] In addition, new porphyrinic metal–organic frameworks with interesting catalytic activity, light-collecting ability, or ionic conductivity have also been explored and showed great potential for future development and practical application.[17] For example, the materials are studied in various fields such as alternative materials for electroluminescent, solar cell, conductive materials, and medicine applications.[18-20] Also some dendronized metalloporphyrin materials were reported to show efficient energy transfer.[21]

Catalytic oxidation of alkenes represents an important industry process.[22] Among different raw materials, cyclohexene is a kind of cheap and easily available industrial one, which can form many different products under different catalysts and reaction conditions.[23] The oxidation products of cyclohexene have various structures, including many important intermediates.[24] Because of the very active epoxy group in cyclohexene oxide, it can react with amine, phenol, alcohol and carboxylic acid to form a series of high value-added compounds, which makes the design of selective catalysts for oxidation of cyclohexene especially crucial. Realizing epoxidation catalysis is tandem oxygen transfer process, Zhong et al.[25] synthesized hollow CoMo oxide. The epoxidation reaction product of cyclohexene was proved to be 1, 2-epoxy-cyclohexane. Kumar et al.,[26] created a β-octachlorovanadylporphyrin materials as a highly efficient and selective catalyst of olefins epoxidation. The yield of epoxides could reach 99%. Farokhi and Hosseini-Monfared[27] prepared chiral catalysts Fe_3O_4/tart/Mn(TCPP)Cl by magnetic separation, and the epoxide yield was increased to 86%.

Here we designed and obtained a new metalloporphyrin compound $Mo_2O_4(C_{48}H_{28}N_4O_8)\cdot(CH_3)_2NH\cdot5H_2O\cdot2DMF$ (Mo_2TCPP). The reason for choosing molybdenum and H_4TCPP ligand for the study is mainly because both molybdates and metalloporphyrin compounds show good catalytic oxidation activity. Oxidants of cyclohexene oxide can be simply classified into the following categories:[28] chemical oxidant, t-BuOOH, hydrogen peroxide and molecular oxygen. Hydrogen peroxide is a common oxidant because it is cheap and easy to get. The preparation of reactive oxygen species intermediates in

---

[a] *Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China. E-mail addresses: lify525@nenu.edu.cn; Tel.: +86-0431-85099765; Fax: +86-0431-85099765.*

[b] *Department of Chemistry, University of California, Riverside, California 92521, USA. E-mail: pingyun.feng@ucr.edu*

† Electronic Supplementary Information (ESI) available: XRD, IR, TG, XPS and additional figures of catalytic experiments, crystal data and refinement. CCDC: 1991923. For ESI and crystallographic data in CIF see DOI: 10.1039/x0xx00000x

catalytic oxidation reaction of metal complexes usually requires high temperature and high pressure.[29] With hydrogen peroxide as the oxidant, we found that the selectivity of the target product was not ideal when the newly synthesized Mo_2TCPP was used to catalyze the oxidation of cyclohexene. However, when cumene hydrogen peroxide (CHP) was used as oxidant, the conversion rate of cyclohexene and the selectivity of epoxycyclohexane were both higher than 99%. What's more, the Mo_2TCPP catalyst is chemically stable under the reaction conditions.

Experimental

Materials

All the chemicals were obtained commercially and were not further purified. The ligands were synthesized according to the previous literatures.[7,30-31]

Ligand synthesis

H_4TCPP ligands were synthesized based on previous reports with modifications.[7,30-31] The mixed solution includes propionic acid, pyrrole and methyl p-formylbenzoate. Purple powders were obtained after refluxing the mixture for a certain period of time. The products were successively washed with methanol, ethyl acetate and tetrahydrofuran, and dried for 12 hours.

Synthesis of Mo_2TCPP

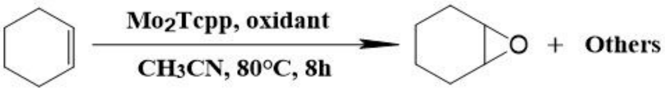
0.05g of $Na_2MoO_4 \cdot 2H_2O$ and 0.02g H_4TCPP were mixed in 3 ml of DMF. The mixture was then left in ultrasound for 30 minutes. Then 1 ml acetic acid was dropped into the solution. All the materials were transferred to a sealed reactor at 150°C for 72 hours. After the reaction was finished, the kettle was naturally cooled to room temperature. Some dark-red crystals were washed by absolute alcohol and dried below 50°C. The final yield was about 71%. Formula: $C_{54}H_{59}Mo_2N_7O_{19}$, Calculated: C, 49.77; H, 4.53; N, 7.53 %; Elemental Analysis: C, 49.70; H, 4.39; N 7.59 %.

Catalytic process

The liquid-phase epoxidation of cyclohexene was carried out in a circular bottom flask immersed in a constant temperature oil bath to maintain the required temperature. The reaction vessel consisted of 30mmol cyclohexene, 20mg catalyst, 10ml acetonitrile and 1ml 1, 2-dimethoxyethane as an internal standard, which were stirred continuously to reach the reaction temperature.[22] Then 30mmol oxidant was added in the mixture and the liquid product was analyzed by gas chromatograph (GC). All oxidation steps are shown in Scheme 1. The catalyst was centrifuged and reused. The conversion and selectivity of the final reaction solution were calculated by the following formula:

$$\text{Conversion}(\%)=\frac{\text{moles of reacted substrate}}{\text{moles of initial substrate}}\times 100\%$$

$$\text{Selectivity}(\%)=\frac{\text{moles of individual product}}{\text{moles of total products}}\times 100\%$$



Scheme 1. The process of oxidation of cyclohexene.

Results and discussion

Single-Crystal structure

Single crystal X-ray diffraction analysis shows that Mo_2TCPP crystallized in the space groups of orthorhombic Pnma. Each molybdenum atom is coordinated with six oxygen atoms, including two bridging oxygen, one terminal oxygen, and three oxygen from two different TCPP ligands. Two Mo atoms form a Mo_2 dimer with the shared bridging oxygen (Fig. 1). Each TCPP ligand coordinates with four different Mo_2 dimers. The geometric structure of macrocyclic porphyrins was planar, and no metal atoms replaced the hydrogen atoms in the center of TCPP. In the porphyrin ligand, the four carboxyl groups acted as junction points, forming a structural skeleton that was perforated. Topologically, Mo_2TCPP can be described as a 3D network with two sub-units, in which both TCPP ligands and each Mo_2 dimer act as four connection nodes (Fig. 2).

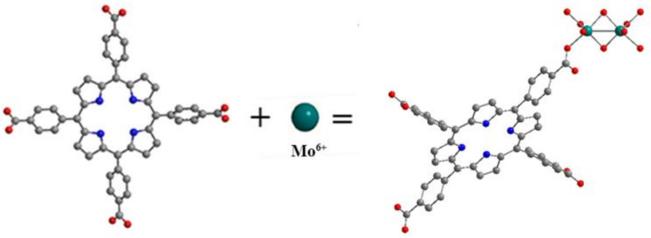


Fig. 1 Reaction scheme for the formation process of Mo_2TCPP.

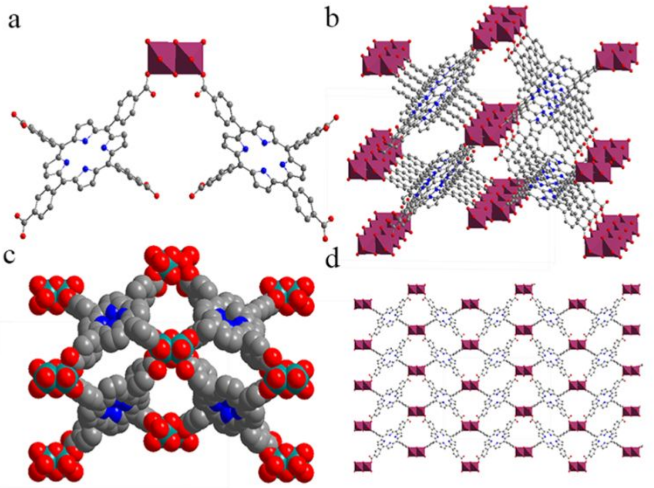


Fig. 2 The structural information of Mo_2TCPP. (a) The topology of the crystalline structure unit and central environment of Mo_2; (b) 3D connection frame for crystal structure; (c) 3D spacing stacking; (d) The vertical topology diagram.

Details of crystal data and structure refinement were listed in Table S1. This structure shows similarity to previously reported structures, MMPF-7 and MMPF-8.[32] MMPF-7 and MMPF-8 were synthesized by Gao et al. with TCPP and tcbpp ligands. In MMPF-7 and MMPF-8, the metal atoms were also coordinated with four nitrogen atoms in the porphyrin ring. While in Mo_2TCPP, no Mo atoms were located in the porphyrin center of TCPP. In our recent reported zirconium metalloporphyrin frameworks, metal ions (Fe^{2+}, Co^{2+}, Zn^{2+}) were also coordinated with N atoms and occupy the center of the ligands.[30] Compared with the polyoxometalate metal-organic framework, TCPP ligand in NNU11 is coordinated with Zn atom instead of Mo atoms.[33] Therefore, the structure of the Mo_2TCPP can be further fabricated with different transition metal ions through bonding with nitrogen atoms at the center of the structure.[34,35]

Thermogravimetric analysis

The crystal sample of Mo_2TCPP was studied by Thermo Gravimetric Analyzer. The sample was heated to 800°C at the rate of 10°C per minute under nitrogen. As shown in Fig. S1, the first step of weight loss at temperature range of 25-154°C was mainly due to the water molecules in the sample. The comparative value difference of mass loss in the range of 20°C to 154°C was about 7.4%, which was in good agreement with the theoretical calculation of water molecules. The organic solvent DMF and the dimethylamine in the structure were decomposed at the temperature range of 155-397°C. Together with the decomposition of the TCPP ligands, the framework was completely decomposed with further temperature increasing.

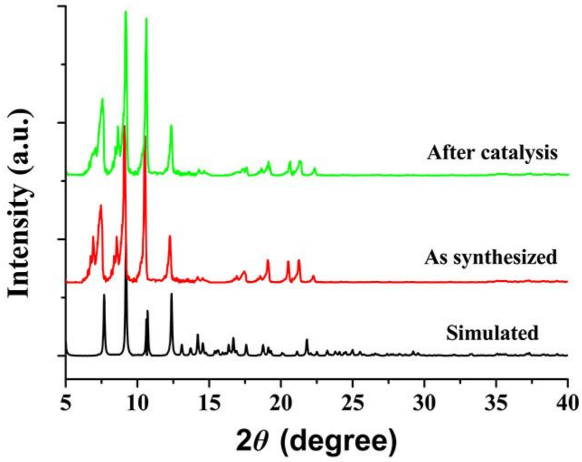


Fig. 3 Powder X-ray diffraction patterns for Mo_2TCPP with CHP as oxidant.

X-ray diffraction patterns

The single crystal data were used to simulate the theoretical PXRD on the software. The measured PXRD curve was consistent with the simulated ones (Fig. 3). And there was no significant change after the catalytic reaction. At the same time, the Mo_2TCPP catalyst was also performed for 10 cycle experiments, and the results were included in the Fig. S2. To test the stability of the catalyst, the newly synthesized crystals were immersed in solutions with different acidity values for 24 hours. From the results of PXRD, we can see that there is no significant change in the catalyst's peak (Fig. 4). So the catalyst was proved to be acid and alkali resistant.

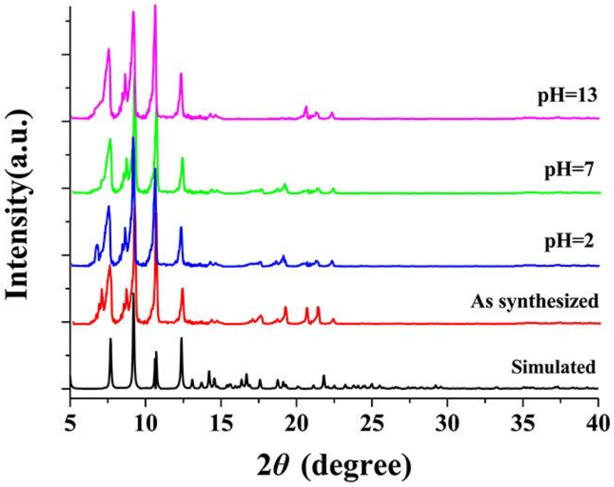


Fig. 4 PXRD patterns of Mo_2TCPP under different conditions, indicating their structural stability upon harsh treatments.

Morphology

According to the results of scanning electron microscopy, it can be clearly seen that Mo_2TCPP are block crystals. The crystal size was measured to be 24 μm × 13 μm × 2.8 μm. Moreover, the crystals did not change significantly after several runs of catalytic reactions. The stability of the catalyst was again demonstrated. EDX and elements mapping (Fig. 5 and Fig. 6) can be used as a reference for the content of crystal elements. The analysis results proved the existence of all the elements that should be present.

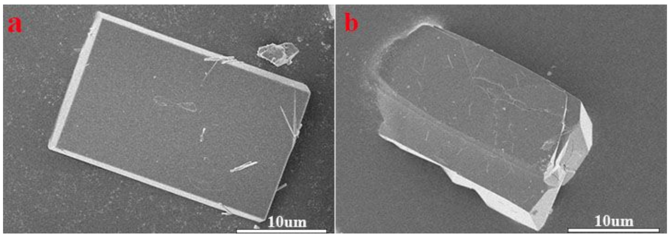


Fig. 5 SEM figures of the newly synthesized Mo_2TCPP (a) and the Mo_2TCPP after catalytic reactions (b).

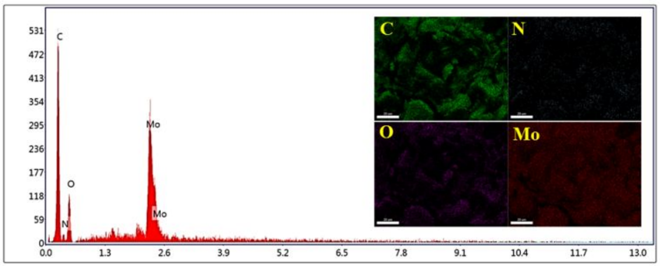


Fig. 6 EDX measurements and elemental mappings of Mo_2TCPP.

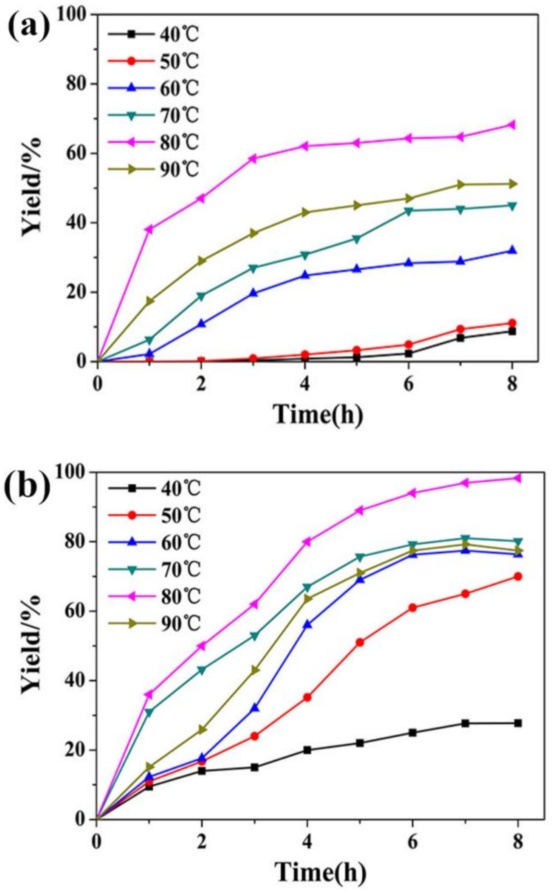


Fig. 7 The productivity of epoxy cyclohexane at different temperatures with H_2O_2(a) and CHP(b) as oxidant.

Catalytic performance and discussion

Solvent properties have important effects on the oxidation process of cyclohexene. Shohreh Farahmand et al. studied the effects of solvents on the oxidation of cyclohexene and found that acetonitrile achieved the maximum conversion rate.[28] Here acetonitrile with moderate polarity and high dielectric constant (36.6) was selected. In Fig. 7, the productivity of epoxy cyclohexane was shown at different temperatures with H_2O_2 and CHP as the oxidants, respectively. With the increase of temperature, the yield of epoxy cyclohexane raise substantially in both cases. The yield of the product reached the maximum value to 99.15% with CHP (68.52% with H_2O_2) at 80°C, and then the yield began to decline as the temperature rose to 90 °C. The reason for this result was H_2O_2 and CHP become unstable at 90°C. The oxidants decomposed rapidly and the by-products in the system increased at higher temperature. In terms of time, the products of the reaction increased rapidly in first three hours. Then it continued to rise slowly and gradually leveled off. The catalytic conversion of cyclohexene by TCPP only was low. But for the sake of comparison, the selectivity of the product was still roughly measurable, as shown in Fig. 8.

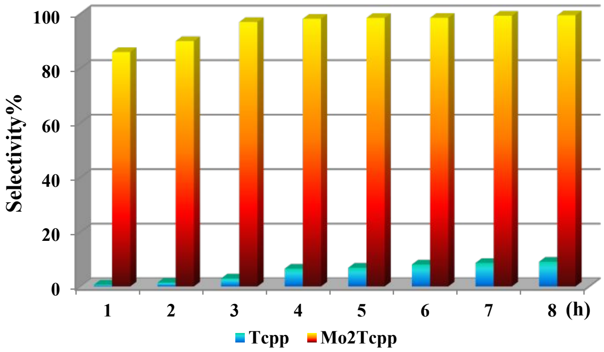


Fig. 8 Selectivity of epoxycyclohexane after catalytic oxidation by TCPP(blue) and Mo_2TCPP at different phases, CHP oxidant .

In order to fully investigate the performance of the catalyst, two starting materials (Na_2MoO_4 and TCPP) for the synthesis of Mo_2TCPP were subjected to catalytic oxidation reaction, and the results were compared with those of Mo_2TCPP, as shown in Table 1. The catalytic oxidation of cyclohexene by different materials has been reported in many literatures. We briefly summarized the results in Table 2. The turnover of a catalytic reaction directly reflects the performance of the catalyst. The crystal reported here showed a high turnover value in experiments and calculations, which was about 1943 (Fig. S3).

Table 1 The selective oxidation of cyclohexene catalyzed by different materials for the information of epoxycyclohexane [a].

Sample Name	Conversion(%)[b]	Selectivity(%)[b]	TON[c]	TOF[d]
$Na_2MoO_4.2H_2O$	9	-	-	-
H_4TCPP	8	-	-	-
Mo_2TCPP	>99	>99	1943	243

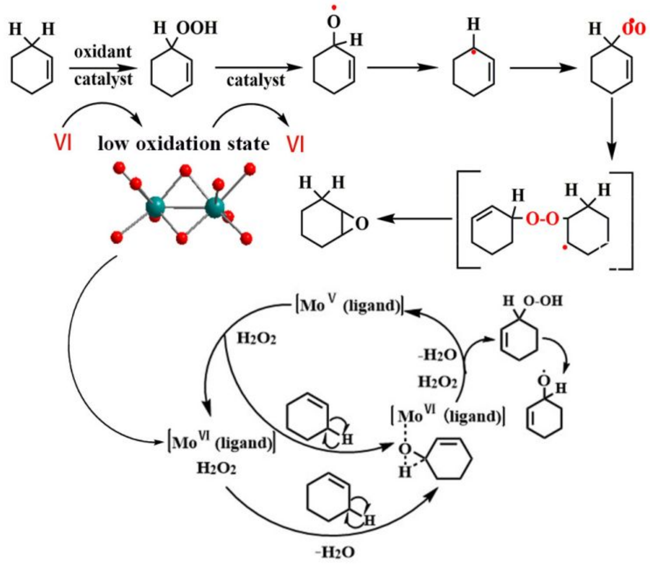
[a] Cyclohexene (30mmol), catalyst (20mg), CHP (30mmol) and acetonitrile(10ml) were stirred at 80°C for 8h. [b] Conversion(%) and Selectivity(%) were determined by GC on an Agilent Technologies 7820A. [c] TON is the ratio of moles of epoxycyclohexane to moles of Mo_2TCPP. [d] TOF is the ratio of moles of products to moles of Mo_2TCPP per unit time(h).

Table 2. Comparison of oxidation of cyclohexene with some literatures.

Entry	Reported Catalyst	Oxidizing agent	Yield(%)	References
1	$CoMoO_4$	O_2	33	R[25]
2	Mn(TCPP)OAc (Bulk)	O_2	28	R[29]
3	CoTM4PyP/MT	O_2	69.5	R[36]
4	MnTPPCl/Co(OAc) $_2$	O_2	72	R[37]
5	Mo_2TCPP	CHP	99.1	this work
6	[VO(hasen)]-Y complex	H_2O_2	50	R[38]
7	A-40Si/Ti-MCM-36(E)	t-BuOOH	58	R[39]
8	A-Si/Ti-MCM-36	t-BuOOH	38	R[40]
9	Mo_2TCPP	H_2O_2	68.5	this work
10	[LFe(NO_3)]	H_2O_2	12	R[41]
	L(RuCl)	H_2O_2	13	R[41]

In order to further explore the scope of the catalytic system of the catalyst Mo_2TCPP, preliminary catalytic oxidation of benzene and cyclooctane were also performed under optimized conditions. And the results were shown in Table S2 and Table S3. In terms of the yield and selectivity of the products, the performance of the catalyst is also suitable for the two oxidation reactions. Our group will follow the progress of these kinds of reactions.

Reaction mechanism hypothesis



Scheme 2 Inference of the reaction mechanism.

In the above reaction (Scheme 2), the oxidant was activated by Mo_2TCPP. The oxidants combined with cyclohexene molecules containing active hydrogen to form peroxides. At the same time, the higher-valence metal ion Mo^{VI} was reduced to the lower-valence metal ion Mo^{V}. Subsequently, the oxidation radical 3-cyclohexene was formed by the interaction between the peroxide and the catalyst. Then the 3-cyclohexene free radical was produced under the action of oxidant. The substrate cyclohexene molecules combine with the cyclohexene peroxide to form a transition state product, but this transition state was unstable and immediately decomposes into epoxycyclohexane.

Conclusions

A new metalloporphyrin material was synthesized. The obtained catalyst Mo_2TCPP showed high selective oxidation of cyclohexene, among which the selevtivity of cyclohexene to epoxy cyclohexane was 99.15%. The use of Mo_2TCPP greatly facilitated the formation of cyclohexene oxide. The effects of different temperature, time and substrate on the reaction were investigated in details. Through a series of comparative experiments, the optimal reaction conditions were found. These are 0.02g Mo_2TCPP, 30mmol CHP, 30mmol cyclohexene, and 10ml of acetonitrile at 80 degrees for 8 hours. The new metalloporphyrin Mo_2TCPP can be recycled and reused at least 10 times without obvious loss of activity. It is expected that this work will contribute to the wide study of these metal-porphyrin ligands for the construction of functional metalloporphyrin skeletons. Our ongoing work includes the custom design of additional porphyrin-based ligands for the construction of functional metalloporphyrin. The applications of new catalytic materials in other reaction systems are also explored.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are thankful for the financial support from the Natural Science Foundation of China (Grant No. 21571029 and 21671035). The synthesis of the material was funded by the US Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Award No. DE-SC0010596 (P.F.).

Notes and references

1 P. Zhang, J. Hu, B. Liu, J. Yang and H. Hou, *Chemosphere*, 2019, **219**, 617-635.
2 M. E. Kosal, J. H. Chou, S. R. Wilson and K. S. Suslick, *Nat. Mater.* , 2002, **1**, 118-121.
3 M. Shmilovits, Y. Diskin-Posner, M. Vinodu and I. Goldberg, *Cryst. Growth Des*.,2003, **3**, 855-863.
4 H. Chung, P. M. Barron, R. W. Novotny, H.-T. Son, C. H and W. Choe, *Cryst. Growth Des*.,2009, **9**, 3327-3332.
5 O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J .Am. Chem. Soc.*, 2011,**133**, 5652-5655.
6 W. Morris, B. Volosskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.,* 2012, **51**, 6443–6445.

7 D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem. Int. Ed*., 2012, **51**, 10307-10310.

8 C. Zou, T. f. Zhang, M. H. Xie, L. j. Yan, G. Q. Kong, X. L. Yang, A. Ma and C. D. Wu, *Inorg. Chem.,* 2013, **52**, 3620−3626.

9 Y. Chen, T. Hoang and S. Q. Ma, *Inorg. Chem.*, 2012, **51**, 12600−12602.

10 A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angew. Chem. Int. Ed*., 2012, **51**, 7440–7444.

11 A. Fateeva, J. Clarisse, G. Pilet, J. M. Grenèche, F. Nouar, B. K. Abeykoon, F. Guegan, C. Goutaudier, D. Luneau, J. E. Warren, M. J. Rosseinsky and T. Devic, *Cryst. Growth Des.,* 2015, **15**, 1819−1826.

12 Y. Diskin-Posner, Goutam K. Patra and I. Goldberg, *Eur. J. Inorg. Chem.*, 2001, **2001**, 2515-2523.

13 T. K. Chandrashekar and S. Venkatraman, *Acc. Chem. Res.*, 2003, **36**, 676-691.

14 H. J. Lu and X. P. Zhang, *Chem. Soc. Rev.*, 2011, **40**, 1899-1909.

15 E. Rose, A. Lecas, M. Quelquejeu, A. Kossanyi and B. Boitrel, *Coord. Chem. Rev.*, 1998, **178-180**, 1407-1431.

16 B. Xu, E. Sheibani, P. Liu, J. B. Zhang, H. N. Tian, N. Vlachopoulos, G. Boschloo, L. Kloo, A. Hagfeldt and L. C. Sun, *Adv. Mater.*, 2014, **26**, 6629-6634.

17 J. A. Johnson, X. Zhang, T. C. Reeson, Y. S. Chen and J. Zhang, *J .Am. Chem. Soc.*, 2014, **136**, 15881-15884.

18 X. L. Chen, R. M. Yu, Q. K. Zhang, L. J. Zhou, C. Y. Wu, Q. Zhang and C. Z. Lu, *Chem. Mat.*, 2013, **25**, 3910-3920.

19 J.-S. Li, Z. Qiu and C.-J. Li, *Adv. Synth. Catal.*, 2017, **359**, 3648-3653.

20 Z.-L. Li, A. Lv, L. Li, X.-X. Deng, L.-J. Zhang, F.-S. Du and Z.-C. Li, *Polym.*, 2013, **54**, 3841-3849.

21 S. M. Rojas-Montoya, M. Vonlanthen, P. Porcu, G. Flores-Rojas, A. Ruiu, D. Morales-Morales and E. Rivera, *Dalton Trans.,* 2019, **48**, 10435–10447.

22 M. Zerrouki, S. Boudjema, A. Choukchou-Braham and I. Rekkab-Hammoumraoui, *New J. Chem.*, 2018, **42**, 16287-16296.

23 V. Smeets, C. Boissière, C. Sanchez, E. M. Gaigneaux, E. Peeters, B. F. Sels, M. Dusselier and D. P. Debecker, *Chem. Mat.*, 2019, **31**, 1610-1619.

24 H. Cao, B. R. Zhu, Y. F. Yang, L. Xu, L. Yu and Q. Xu, *Chin. J. Catal*., 2018, **39**, 899–907.

25 W. Zhong, M. Liu, J. Dai, J. Yang, L. Mao and D. Yin, *Appl. Catal.,B*, 2018, **225**, 180-196.

26 R. Kumar, N. Chaudhary, M. Sankar and M. R. Maurya, *Dalton Trans.*, 2015, **44**, 17720-17729.

27 A. Farokhi and H. Hosseini-Monfared, *New J. Chem.*, 2016, **40**, 5032-5043.

28 S. Farahmand and M. Ghiaci, *Microporous Mesoporous Mater.*, 2019, **288**.

29 S. Rayati, N. Pournaser, F. Nejabat and P. Nafarieh, *Inorg. Chem. Commun.*, 2019, **107**.

30 Q. Lin, X. Bu, A. Kong, C. Mao, X. Zhao, F. Bu and P. Feng, *J. Am. Chem. Soc.*, 2015, **137**, 2235-2238.

31 S. Yuan, J. S. Qin, L. Zou, Y. P. Chen, X. Wang, Q. Zhang and H. C. Zhou, J. Am. Chem. Soc, 2016, **138**, 6636-6642.

32 W.-Y. Gao, Z. Zhang, L. Cash, L. Wojtas, Y.-S. Chen and S. Ma, *CrystEngComm*, 2013, **15**.

33 Q. Huang, T. Wei, M. Zhang, L.-Z. Dong, A. M. Zhang, S.-L. Li, W.-J. Liu, J. Liu and Y.-Q. Lan, *J. Mater. Chem. A*, 2017, **5**, 8477-8483.

34 Y. Diskin-Posner and I. Goldberg, *New J. Chem.*, 2001, **25**, 899-904.

35 W. Zhao, W. Wang, J. Peng, T. Chen, B. Jin, S. Liu, W. Huang and Q. Zhao, *Dalton Trans.*, 2019, **48**, 9631-9638.

36 H. Kameyama, F. Narumi, T. Hattori and H. Kameyama, *J. Mol. Catal. A:Chem*, 2006, **258**, 172-177.

37 Y. Li, X.-T. Zhou and H.-B. Ji, *Catal. Commun.*, 2012, **27**, 169-173.

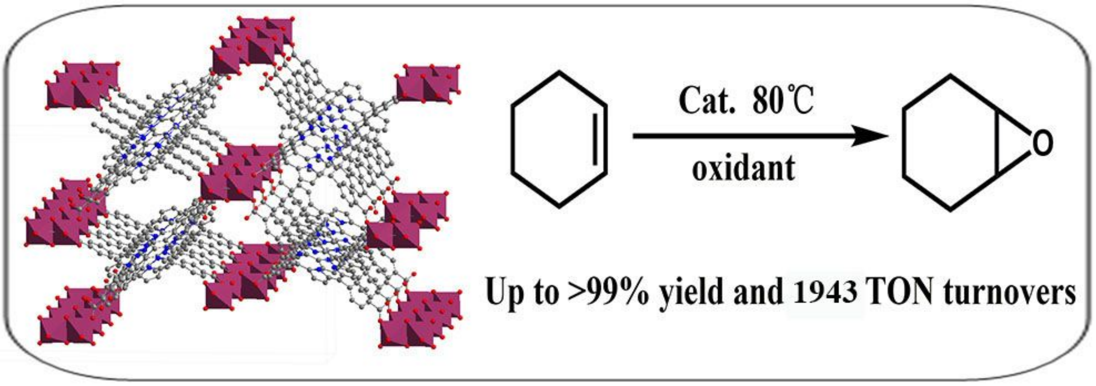
38 D. R. Godhani, H. D. Nakum, D. K. Parmar, J. P. Mehta and N. C. Desai, *J. Mol. Catal. A: Chem*, 2016, **415**, 37-55.

39 F. Jin, C.-C. Chang, C.-W. Yang, J.-F. Lee, L.-Y. Jang and S. Cheng, *J. Mater. Chem. A*, 2015, **3**, 8715-8724.

40 F. Jin, S. Huang, S. Cheng, Y. Wu, C.-C. Chang and Y.-W. Huang, *Catal. Sci. Technol.*, 2015, **5**, 3007-3016.

41 D. R. Godhani, H. D. Nakum, D. K. Parmar, J. P. Mehta and N. C. Desai, *J. Mol. Catal. A:Chem*, 2017, **426**, 223-237.

The first 3D molybdenum-porphyrin framework was synthesized and structurally characerized, showing perfect catalytic activity in oxidation of cyclohexene.



Up to >99% yield and 1943 TON turnovers