有机化学 DOI: 10.6023/cjoc202008032 研究论文
Chinese Journal of Organic Chemistry ARTICLE

聚硒醚催化环己烯氧化制备 1,2-环己二醇

黄杰军[a,c] 钱蓉蓉[b] 王 爽[a] 曹洪恩*[,a]
([a]扬州大学园艺与植物保护学院 江苏扬州 225009)
([b]江苏旅游职业学院 江苏扬州 225127)
([c]江苏扬农化工集团有限公司 江苏扬州 225009)

摘要 开发了一种一步合成聚硒醚的新方法, 该材料可用于催化环己烯二羟化合成重要的化工中间体环己二醇, 是一种高效并可回收的催化剂. 有趣的是, 该材料在分子层面的独特结构, 使得相关反应以自由基机理进行, 并可使用分子氧作为部分氧化剂, 这与之前许多报道的硒催化反应有所不同.

关键词 硒; 聚硒醚; 环己烯; 1,2-环己二醇; 绿色氧化

Polyselenide-Catalyzed Cyclohexene Oxidation to Produce 1,2-Cyclohexanediol

Huang, Jiejun[a,c] Qian, Rongrong[b] Wang, Shuang[a] Cao, Hong'en*[,a]
([a] *School of Horticulture and Plant Protection, Yangzhou University, Yangzhou, Jiangsu 225009*)
([b] *Jiangsu College of Tourism, Yangzhou, Jiangsu 225127*)
([c] *Jiangsu Yangnong Chemical Group Co. Ltd, Yangzhou, Jiangsu 225009*)

Abstract A new method for one-step synthesis of polyselenide was developed. The material was found to be an efficient and recyclable catalyst for the dihydroxylation of cyclohexene to produce 1,2-cyclohexanediol, which was an important intermediate for the synthesis of many fine chemicals. Interestingly, the unique structure of the catalyst at molecular level resulted in a novel free-radical reaction methanism allowing the utilization of O_2 as the supplementary oxidant, which was quite different from most of the reported organoselenium-catalyzed reactions.

Keywords selenium; polyselenide; cyclohexene; 1,2-cyclohexanediol; green oxidation

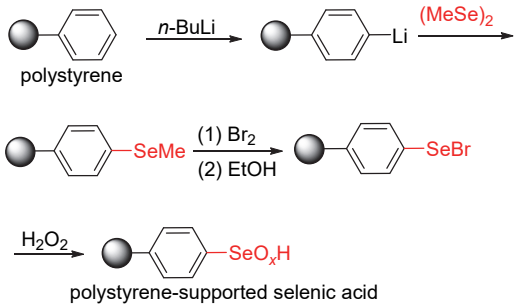
1 Introduction

Chalcogen elements possess unique features for their large atomic radiuses weakening the binding forces of their outlier electrons.[1] Recently, selenium-containing materials have drawn much attention for their good chemical- and bio-activities endowing the wide applications in many fields, such as biochemistry,[2] organic synthesis,[3] and materials science.[4] With the rapid development of the investigations on organoselenium catalysis,[5] a variety of selenium-containing materials and reagents have been developed to catalyze reactions to build complex organic skeletons and to achieve green transformations for industrial application purposes.[6] Since the Se—O bond is weak, selenium-containing species, such as the selenic acids and diselenides, are nice oxygen carrier catalysts to transfer oxygen from green oxidants into the useful fine chemical products.[7] In comparison with traditional metal catalysts,[8] selenium is even cheaper (99.99% purity Se powder is *ca.* \$60/kg in China) and is metabolizable for human beings.[9] It is also more tolerable according to the latest revision of the U.S. Pharmacopeia's New Standard and Method for Elemental Impurities Control in 2017.[10]

Yet, the selective oxidation of cyclohexene is a significant reaction in industry.[11] It may produce 7-oxabicyclo-[4.1.0]heptane, cyclohexane-1,2-diol, adipic acid, cyclohex-2-en-1-ol and cyclohex-2-en-1-one, among which, cyclohexane-1,2-diol is an especially important product because it is the key intermediate for producing many useful fine chemicals such as pyrocatechol, cyclohexane-1,2-

* Corresponding author. E-mail: hecao@yzu.edu.cn
Received August 18, 2020; revised September 26, 2020; published online December 18, 2020.
Project supported by the National Key Research and Development Program of China (No. 2018YFD0200100) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.
国家重点研发计划(No. 2018YFD0200100)和江苏省高校优势学科建设工程资助项目.

dione, 1,2-dichlorocyclohexane, adipaldehyde, *etc*.[12] In line with calls for environment protection, the transition-metal free reactions are in rapid development.[13] In the field, the organoselenium-catalyzed dihydroxylation reaction of alkenes was initially reported by Santi *et al*.[14] and the technique was then applied in the dihydroxylation of cyclohexene to produce *trans*-cyclohexane-1,2-diol.[12,15] The reaction could be catalyzed by heterogeneous polystyrene-supported selenic acid catalyst, which was recyclable to reduce the cost for potential industrial-grade applications.[16] However, tedious fabrication procedures of the catalyst including the polymer lithiation, selenization, bromination and oxidation enhanced its cost and might cause heavy pollution for large-scale applications (Scheme 1).[16] Herein, we wish to report a novel polyselenide-catalyzed cyclohexene dihydroxylation to produce *trans*-1,2-cyclohexanediol, and in comparison with polystyrene-supported selenic acid catalyst, the polyselenide catalyst can be synthesized in just one step from easily accessible starting materials.



Scheme 1 Synthesis of the polystyrene-supported selenic acid catalyst for cyclohexene dihydroxylation

2 Results and discussion

2.1 Preparation and characterization of catalyst

Se—C bond can be formed via the S_N2 reaction of SeH with C(sp^3)—Cl. To build the polymer chain, dihalohydrocarbon was employed as the starting material, while NaHSe, a dinucleophile, was employed as the selenization reagent. NaHSe could be generated via the reduction of Se powder with $NaBH_4$ and was directly used without separation. Through the selenization method, a series of polyselenides were synthesized from the corresponding dihalohydrocarbons (Figure 1a).[6a,6e] In solid ^{13}C NMR spectrum of the polyselenide being prepared from 1,4-bis(chloromethyl)benzene monomer, the aryl carbons presented their signals at δ 140.5, 131.2 and 130.1, respectively, while the benzyl carbon signals were at δ 30.5 and 24.3. The signal of selenium in ^{77}Se NMR was at δ 424.1, which was in accordance with the predicted value of the selenium signal in selenide. Moreover, the energy dispersive X-ray (EDX) analysis of the material attested the existence of selenium, while elemental mappings showed that the selenium sites (in purple color in the picture) dispersed on the surface of the carbon skeleton (in red color in the picture) of the material (Figure 1b), and this might facilitate the catalyzed reactions in further applications.

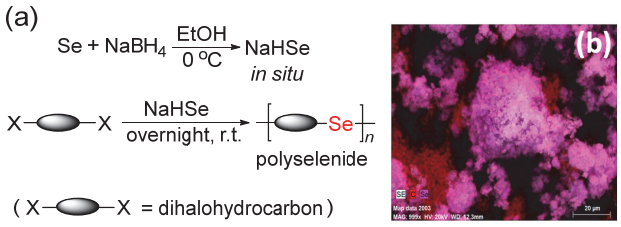
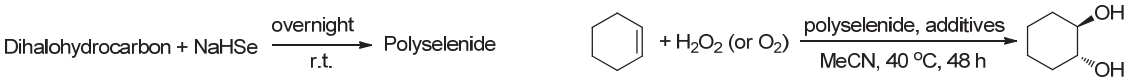


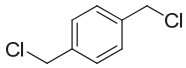
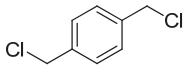
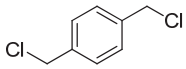
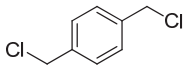
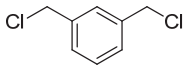
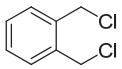
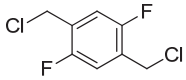
Figure 1 (a) Preparation steps and (b) element mapping of the polyselenide being synthesized from 1,4-bis(chloromethyl)benzene

2.2 Catalyst screening

The materials were then employed as the catalyst for cyclohexene dihydroxylation to produce *trans*-cyclohexane-1,2-diol. A series of parallel experiments were performed to screen out the preferable catalyst and optimize the reaction conditions and the results are summarized in Table 1. Catalyzed by the polyselenide fabricated from 1,4-bis(chloromethyl)benzene, the oxidation of cyclohexene with H_2O_2 could produce *trans*-cyclohexane-1,2-diol in 86% yield (Table 1, Entry 1). It was notable that the reaction utilized O_2 as partial oxidant, so that the amount of H_2O_2 could be obviously reduced in comparison with the reported works.[12,15] Control experimental results as well as the reference reports[16-17] well supported the hypothesis that O_2 participated the reaction, and the O_2-mediated reaction was obviously promoted by water (Table 1, Entries 2 vs. 3). Moreover, an isotope labeled experiment was performed in a $^{18}O_2$ charged Schlenk tube and the mixture was analyzed by gas chromatograph-mass spectrometer (GC-MS) after reaction. By calculating the peak area ratio, it was found that the obtained product contained some single-^{18}O-labeled *trans*-cyclohexane-1,2-diol (M=118, peak area accounted for 7.6%), while double-^{18}O-labeled product (M=120) was not observed. This result well confirmed that the molecular oxygen could participate the reaction and was kept in product, and only one oxygen in product was from O_2 at the maximum. The minimum amount of H_2O_2 was found to be 90 mol%, otherwise, both cyclohexene conversion and product yield decreased (Table 1, Entries 4 vs. 1). Polyselenides prepared from 1,3-bis(chloromethyl)benzene or 1,2-bis(chloromethyl)benzene were found to be less reactive (Table 1, Entries 5, 6), probably due to their crooked polymer chain hindering the contact of the reactants. In reported works, it has been found that introducing electron-withdrawing groups into the organoselenium catalysts could enhance their activities because the electron-withdrawing effect enhanced the positive charges of the catalytic selenium centres to promote the ionic reactions occurring via an electrophilic addition of the selenium cation first.[12] However, in this reaction, using electron-deficient polyselenide catalyst resulted in decreased product yield on the contrary (Table 1, Entry 7), showing that the polyselenide-catalyzed reaction might proceed via a completely new reaction route.[12,15]

Table 1 Parallel experiments of the polyselenide-catalyzed dihydroxylation reactions of cyclohexene[a]



Entry	Dihalohydrocarbon[b]	Oxidant/Additive	Conversion/%[c]	Yield/%[d]
1		90 mol% H_2O_2, O_2/—	88	86
2		O_2/—	6	5
3		O_2/200 mol% H_2O	17	16
4		80 mol% H_2O_2, O_2/—	77	76
5		90 mol% H_2O_2, O_2/—	80	79
6		90 mol% H_2O_2, O_2/—	72	70
7		90 mol% H_2O_2, O_2/—	76	74

[a] 20 mmol of cyclohexene, 100 mg of polyselenide and 2 mL of MeCN were used; the reactions were performed under 101 kPa O_2. [b] Dihalohydrocarbons used in polyselenide preparations. [c] Conversion ratio of cyclohexene. [d] GC-yield of *trans*-1,2-cyclohexanediol calculated on the basis of the internal standard curve.

2.3 Recycle and reuse of catalyst

Testing with potassium iodide-starch test paper showed that no H_2O_2 left after reaction, indicating that it was relatively safe to separate the product via distillation. Moreover, the oxidation product of MeCN was not observed in the small-scale reaction under mild conditions (40 ℃) and a series of references have reported that in Se-catalyzed reactions, MeCN was a commonly used solvent when using H_2O_2 as solvent.[18] Thus, a magnified reaction in 0.5 mol scale was performed in MeCN, and the product was isolated by distillation under reduced pressure in 81% yield (100～103 ℃ at 800 Pa pressure). The recycled catalyst could be reused for at least five times without deactivation (Figure 2a). Scanning electron microscope (SEM) images demonstrate that there are little changes in morphologies of the material after the 5th cycle of reaction (Figures 2b vs. 2c).

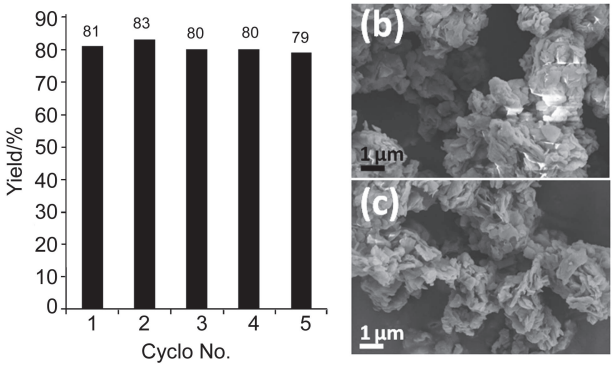


Figure 2 Catalyst recycle and reuse (a) and the SEM images of the polyselenide before (b) and after (c) the 5th cycle of reaction

In comparison with reported works,[14,16] this method could prepare *trans*-cyclohexane-1,2-diol with enhanced atom utilization ratio. Methods reported in Refs. [13, 15] were taken for example to compare with the reaction of this work and their atom utilization ratios were calculated (Table 2). Because solvents could be recovered in large-scale production, they were not included in the calculation process. The clean and cheap components, such as water and O_2 (or air[16]) were also ignored in calculation. In order to prepare 1 mmol of *trans*-cyclohexane-1,2-diol, the $(PhSe)_2$-catalyzed method reported in Ref. [14] consumed 493.0 mg of starting materials (Table 2, Entry 1), while for the polystyrene-supported selenic acid-catalyzed reaction reported in Ref. [16], *ca.* 149.8 mg of starting materials were consumed (Table 2, Entry 2). In this work, only 142.9 mg of materials were consumed for preparing 1 mmol of *trans*-cyclohexane-1,2-diol (Table 2, Entry 3). Moreover, the polyselenide catalyst in this work could be synthesized in just one step, which was more concise than the tedious steps in Ref. [16], and the reaction scale in this work (500 mmol cyclohexene scale) was even larger than both Ref. [14] and Ref. [16] (1 mmol cyclohexene scale). Therefore, the method herein is much more practical than reported works from both sustainable chemistry and industrial application viewpoints.

2.4 Reaction mechanism study

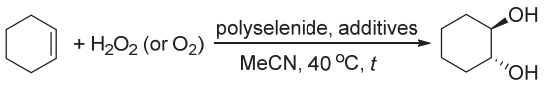
Control experiments were performed for mechanism study. Addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or hydroquinone as the free radical scavenger

Table 2 Comparison of the work with reported references on atom economy

Entry	Ref.	Consumed weight of starting materials vs. product/(mg•mmol^{-1})
1	[14]	493.0
2	[16]	149.8
3	This work	142.9

restrained the transformation (Table 3, Entries 1, 2), while the free radical initiator azodiisobutyronitrile (AIBN) obviously accelerated the reaction process (Table 3, Entries 3 vs. 4). Therefore, it attested that the polyselenide-catalyzed reaction might occurred in a free radical mechanism [19] other than the reported ionic reaction route.[12,15] In the control experiment using stoichiometric amount of H_2O_2 in N_2 atmosphere, the product yield decreased to 79% (Table 3, Entry 5 vs. Table 1, Entry 1), showing that H_2O_2 might partially decompose during the reaction process and O_2 was an essential supplementary oxidant to ensure a full conversion. Moreover, the reaction of cyclohexene with oxidation state polyselenide (oxidized by O_2) in N_2 could produce *trans*-cyclohexane-1,2-diol in 38% yield, showing that O_2 could participate the reaction as an additional oxidant (Table 3, Entry 6).

Table 3 Control experiments for mechanism study[a,b]



Entry	Oxidant/additve	*t*/h	Conversion/%	Yield[c]/%
1	90 mol% H_2O_2, O_2/TEMPO (100 mol%)	48	0	0
2	90 mol% H_2O_2, O_2/Hydroquinone (100 mol%)	48	0	0
3	90 mol% H_2O_2, O_2/AIBN (100 mol%)	24	88	78
4	90 mol% H_2O_2, O_2	24	67	66
5	100 mol% H_2O_2, N_2	48	81	79
6	N_2/200 mol% H_2O[d]	48	42	38

[a] 20 mmol of cyclohexene, 100 mg of polyselenide and 2 mL of MeCN were used. [b] The reactions were catalyzed by the polyselenide being prepared from 1,4-bis(chloromethyl)benzene monomer. [c] GC-yield of *trans*-1,2-cyclohexanediol calculated on the basis of the internal standard curve. [d] 500 mg of O_2 treated polyselenide was employed.

As being attested by the X-ray photoelectron spectroscopy (XPS) analysis, polyselenide could be oxidized into its oxidation state involving Se(IV) by H_2O_2 (Figure 3a). Flourier IR spectrum of the used catalyst showed that OH (*ca.* 3100～2800 cm^{-1}) groups were introduced into the material after reaction (Figure 3b, red line vs. black line). The peak in the IR spectrum of the used catalyst at 1699 cm^{-1} attributed to C=O, which reflected the oxidation of benzyl CH_2 of the material adjacent to selenium, but no Se=O signals were observed in the IR spectrum of the material after reaction (Figure 3b, red line). Thus, it was supposed that the Se(IV) moieties with hydroxyls were involved in the materials after the reaction. Moreover, the hydroxyl radical in the reaction process could be captured by salicylic acid. As showing in Figure 3c, after adding the reaction liquid, a strong adsorption at around 490～550 nm (520 nm at maximum) was observed in the UV-Vis spectra (red curve vs. black curve), which was the characteristic peak of the adducts of hydroxyl radical with salicylic acid (*i.e.* 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid) reflecting the existence of hydroxyl radical.[20]

Based on the above experimental results and reference reports,[6a,16,19,21-23] a plausible mechanism was supposed (Scheme 2). First, as being indicated by the results of control experiment, the reaction occurred via a free radical reaction mechanism, and hydroxyl radical was the most probable active species (Scheme 2, a).[6a,19] In the course, polyselenide was initially oxidized into its oxidation state species (**A**).[21] Compared with the reported polystyrene-supported selenic acid,[16] the selenium site in polyselenide bears double bulky aryls preventing its sufficient contact with cyclohexene (Scheme 2, b). Thus, the polyselenide-catalyzed reaction did not occur via ionic mechanism, which required the direct contact of the catalytic selenium site with cyclohexene. In the reaction, the Se—O scission in **A** could produce hydroxyl radicals and the catalyst was converted into its radical state (**B**), which captured hydrogen under the aqueous conditions and produced the hydroxyl free radical (Scheme 2, a). Polyselenide **C** with Se—H was active and could be oxidized by H_2O_2 or even O_2 to Se—OH and restart the next hydroxyl free radical prod-

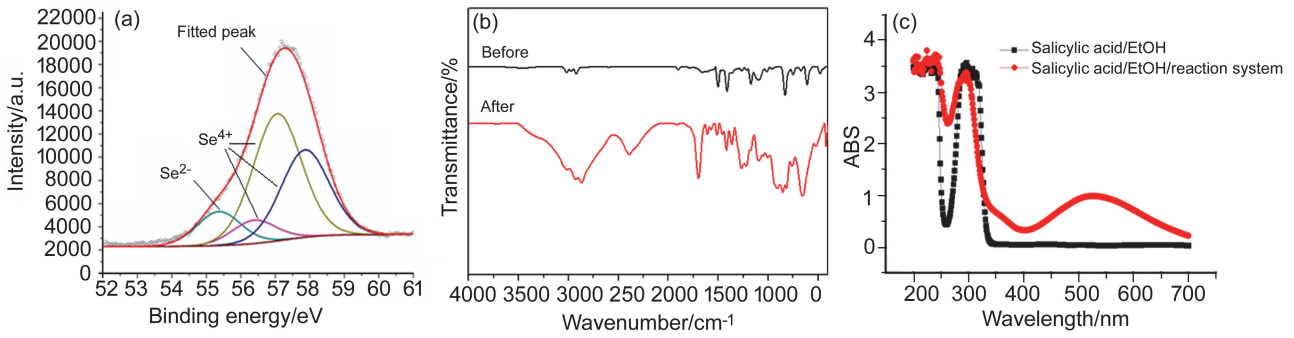
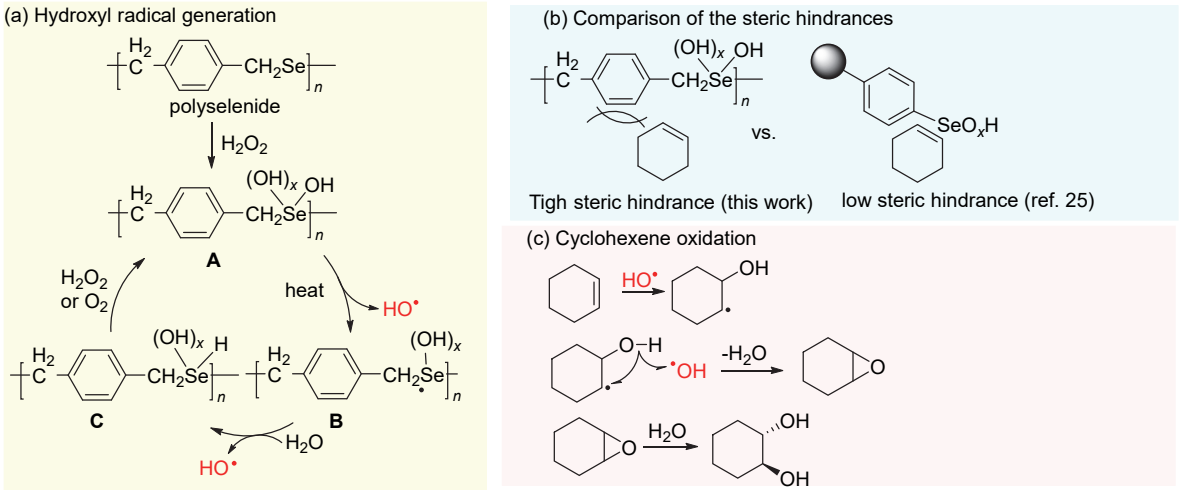


Figure 3 (a) XPS spectrum of the used catalyst, (b) IR spectra of the polyselenide before and after the reaction and (c) hydroxyl radical capture by salicylic acid via UV-Vis detection



Scheme 2 Plausible mechanism of the Se-polymer-catalyzed oxidation of cyclohexene

ucing cycle.[6a,22-23] In the cyclohexene dihydroxylation reaction (Scheme 2, c), addition of hydroxyl radical to cyclohexene afforded the intermediate 2-hydroxyl cyclohexyl radical, which then led to the epoxide (*i.e.* 7-oxabicyclo[4.1.0]heptane).[14,16] Hydration of the epoxide produced *trans*-1,2-cyclohexane-1,2-diol via the attack of water from the backside of the intermediate. Removing polyselenide catalyst after 24 h reaction, it produced *trans*-1,2-cyclohexane-1,2-diol in 72% yield after 48 h (total reaction time), showing that the continuous generation of hydroxyl free radical by polyselenide was essential for the reaction.

3 Conclusions

In conclusion, we have designed and prepared polyselenide, which, as a selenium-containing polymer, was catalytically active for the dihydroxylation reaction of cyclohexene to produce the important industrial intermediate *trans*-1,2-cyclohexanediol. In comparison with the reported polystyrene resin-supported selenic acid, this material could be prepared in just one step and its unique structures resulted in a completely different reaction route, allowing the use of O_2 as partial oxidant so that the used H_2O_2 amount could be reduced. The product yield was good, while no wastes were generated during the process. This novel polyselenide material may be applied as a good catalyst for transfering oxygen from cheap and clean oxidants into high value-added products for industrial purpose.[24] The investigations of smart techniques involving selenium and oxidation reactions with molecular oxygen are booming in recent years.[25]

4 Experimental section

4.1 General methods

Infrared (IR) spectra were determined on a Bruker Tensor 27 IR spectrometer. Liquid-state NMR spectra were recorded on a Bruker Avance III 400 nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR spectroscopy and 100 MHz for ^{13}C NMR spectroscopy) by using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Solid-state NMR spectra were recorded on a Bruker Avance III 400WB nuclear magnetic resonance spectrometer (100 MHz for ^{13}C NMR and 76.28 MHz for ^{77}Se NMR). Melting points (m.p.) were measured with a WRS-2A digital melting point measuring instrument. The scanning electron microscope (SEM) image was determined by a Zeiss Supra55 field emission scanning electron microscope. X-Ray photoelectron spectroscopy (XPS) spectrum was determined by a ThermoScientific ESCALAB 250Xi X-ray photoelectron spectrometer. GC-MS analysis was performed on a ThermoFisher Trace 1300-ISQ LT spectrometer (EI). The yield of *trans*-1,2-cyclohexanediol was determined by GC, with a capillary DB1701 column and flame ionization detector. The oven temperature was programmed at 70～260 ℃ with the heating rate at 30 ℃/min. GC yields were confirmed with benzophenone as the internal standard. The chemical reagents used in this work were all analytically pure and purchased from Energy Chemical. They were directly used without special treatment.

4.2 General procedures for the synthesis of polyselenide

Cooling by ice-water bath, 15 mmol of Se powder and 21 mmol of $NaBH_4$ were added into a 50 mL round bottom flask, which was charged with N_2. 7.5 mL of absolute ethanol was then injected into the flask by syringe and the reaction liquid was magnetically stirred until the disappearance of Se powder (*ca.* 2～3 h). Ice-water bath was removed and 7.5 mmol of dihalohydrocarbon was then injected into the solution containing the *in situ* generated NaHSe. The reaction liquid was stirred overnight and the precipitated polyselenide was isolated by filtration and washed by deionized water and ethanol. After being dried under vacuum for 24 h, 1.34 g of the material of polyselenide was obtained as a powder in light color.

4.3 General procedures for the dihydroxylation reaction of cyclohexene

20 mmol of cyclohexene, 18 mmol of H_2O_2 (30%), 100 mg of polyselenide and 2 mL of MeCN were added into a reaction tube charged with pure O_2 (101 kPa). The tube was

then heated at 40 ℃ for 48 h. The mixture was sent to GC-analysis to determine the yield of *trans*-cyclohexane-1,2-diol. White solid, m.p. 102.5～103.6 ℃ (lit.[16] 102～103 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.35 (s, 2H), 2.93 (s, 2H), 1.97 (t, J=2.8 Hz, 2H), 1.70 (t, J=3.0 Hz, 2H), 1.27～1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.9, 32.9, 24.4.

4.4 Details for recycle and reuse of catalyst

0.5 mol of cyclohexene, 0.45 mol of H_2O_2 (30%), 2.5 g of polyselenide and 50 mL of MeCN were added into a 100 mL round bottom flask charged with pure O_2 (101 kPa). The flask was then heated at 40 ℃ in O_2 atmosphere for 48 h. Then, the catalyst was recycled by filtration and the solvent in the filtrate was removed by distillation under reduced pressure with rotary evaporator. The product in residue was separated by distillation at reduced pressure (100～103 ℃ at 800 Pa). The recycled catalyst could be reused in the next turn of reaction.

4.5 Details for the O-18 labeled experiment.

20 mmol of cyclohexene, 18 mmol of H_2O_2 (30%), 100 mg of polyselenide and 2 mL of MeCN were added into a 25 mL Schlenk tube charged with pure $^{18}O_2$ (101 kPa). The tube was then sealed and heated at 40 ℃ for 48 h. The mixture was sent to GC-analysis showing that the product contained some single-^{18}O-labeled *trans*-cyclohexane-1,2-diol (M=118, peak area accounted for 7.6%), while double-^{18}O-labeled product (M=120) was not observed. The value was calculated by comparison the peak areas of the two product (M=116 and M=118). The equation is: ^{18}O-labeled *trans*-cyclohexane-1,2-diol (M=118) content $=A_{M118}/(A_{M118}+A_{M116})\times100\%$, where A_{M118} is the peak area of single-^{18}O-labeled *trans*-cyclohexane-1,2-diol (M=118), while A_{M116} is that of simple *trans*-cyclohexane-1,2-diol (M=116).

4.6 Details for the reaction of cyclohexene with oxidation state polyselenide

500 mg of polyselenide was initially heated at 40 ℃ in O_2 flow for 10 h to get its oxidation state material, which was then sent to a 20 mL reaction tube with 20 mmol of cyclohexene, 40 mmol of H_2O (0.72 mL) and 2 mL of MeCN. The flask was charged with N_2 and heated at 40 ℃ for 48 h and then sent to GC analysis.

Supporting Information Experimental details of the atom utilization efficiency calculation and the internal standard curve drawing and the analysis spectra of the product and catalyst materials were involved. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] (a) Chen, Y.; Deng, X.; Jing, X.; Zhou, H. *Chin. J. Org. Chem.* **2020**, *40*, 4147 (in Chinese).
(陈颖, 邓鑫, 景峭壁, 周宏伟, 有机化学, **2020**, *40*, 4147.)
(b) Ge, Y.; Kong, J.; Yang, C.; Yang, Q.; Zhang, X. *Chin. J. Org. Chem.* **2020**, *40*, 1760 (in Chinese).
(葛颜玉, 孔晶, 杨成根, 杨倩, 张旭, 有机化学, **2020**, *40*, 1760.)
(c) Bao, W.-H.; He, M.; Wang, J.-T.; Peng, X.; Sung, M.; Tang, Z.; Jiang, S.; Cao, Z.; He, W.-M. *J. Org. Chem.* **2019**, *84*, 6065.
(d) Lu, L.-H.; Wang, Z.; Xia, W.; Cheng, P.; Zhang, B.; Cao, Z.; He, W.-M. *Chin. Chem. Lett.* **2019**, *30*, 1237.
(e) Higashimae, S.; Kurata, D.; Kawaguchi, S.-I.; Kodama, S.; Sonoda, M.; Nomoto, A.; Ogawa, A. *J. Org. Chem.* **2018**, *83*, 5267.

[2] (a) Ruberte, A. C.; Sanmartin, C.; Aydillo, C.; Sharma, A. K.; Plano, D. *J. Med. Chem.* **2020**, *63*, 1473.
(b) Cao, H.; Yang, Y.; Chen, X.; Liu, J.; Chen, C.; Yuan, S.; Yu, L. *Chin. Chem. Lett.* **2020**, *31*, 1887.
(c) Mao, X.; Li, P.; Li, T.; Zhao, M.; Chen, C.; Liu, J.; Wang, Z.; Yu, L. *Chin. Chem. Lett.* **2020**, *31*, 3276.

[3] (a) Wu, C.; Xiao, H.-J.; Wang, S.-W.; Tang, M.-S.; Tang, Z.-L.; Xia, W.; Li, W.-F.; Cao, Z.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 2169.
(b) Goulart, T. A. C.; Kazmirski, J. A. G.; Back, D. F.; Zeni, G. *J. Org. Chem.* **2019**, *84*, 14113.
(c) Liu, M.-X.; Li, Y.-M.; Yu, L.; Xu, Q.; Jiang, X.-F. *Sci. China: Chem.* **2018**, *61*, 294.

[4] (a) Chen, X.; Mao, J.; Liu, C.; Chen, C.; Cao, H.; Yu, L. *Chin. Chem. Lett.* **2020**, *31*, 3205.
(b) Zhu, Z.; Wang, W.; Zeng, L.; Zhang, F.; Liu, J. *Catal. Commun.* **2020**, *142*, 106031.
(c) Cao, K.-H.; Deng, X.; Chen, T.; Zhang, Q.-T.; Yu, L. *J. Mater. Chem. A* **2019**, *7*, 10918.

[5] Singh, F. V.; Wirth, T. *Catal. Sci. Technol.* **2019**, *9*, 1073.

[6] (a) Yu, L.; Cao, H.-E.; Zhang, X.; Chen, Y.; Yu, L. *Sustainable Energy Fuels* **2020**, *4*, 730.
(b) Zheng, Y.-H.; Wu, A.-Q.; Ke, Y.-Y.; Cao, H.-E.; Yu, L. *Chin. Chem. Lett.* **2019**, *30*, 937.
(c) Liu, X.; Liang, Y.-Y.; Ji, J.-Y.; Luo, J.; Zhao, X.-D. *J. Am. Chem. Soc.* **2018**, *140*, 4782.
(d) Depken, C.; Krätzschmar, F.; Rieger, R.; Rode, K.; Breder, A. *Angew. Chem., Int. Ed.* **2018**, *57*, 2459.
(e) Yu, L.; Chen, C. *CN 106432739*, **2017**.

[7] Chen, C.; Cao, Y.-T.; Wu, X.-X; Cai, Y.-L.; Liu, J.; Xu, L.; Ding, K.-H.; Yu, L. *Chin. Chem. Lett.* **2020**, *31*, 1078.

[8] (a) Chen, Y.; Jing, X.; Yu, L. *Chin. J. Org. Chem.* **2020**, *40*, 2570 (in Chinese).
(陈颖, 景峭壁, 俞磊, 有机化学, **2020**, *40*, 2570.)
(b) Yang, Y.; Li, M.; Cao, H.; Zhang, X.; Yu, L. *Mol. Catal.* **2019**, *474*, 110450
(c) Zhao, S.-Y.; Xu, B.-L.; Yu, L.; Fan, Y.-N. *Chin. Chem. Lett.* **2018**, *29*, 884.
(d) Zhao, S.-Y.; Xu, B.-L.; Yu, L.; Fan, Y.-N. *Chin. Chem. Lett.* **2018**, *29*, 475.
(e) Fan, X.; Yi, R.; Wang, F.; Zhang, X.; Xu, Q.; Yu, L. *Chin. J. Org. Chem.* **2018**, *38*, 2736 (in Chinese).
(范昕, 易容, 王芳, 张旭, 徐清, 俞磊, 有机化学, **2018**, *38*, 2736.)
(f) Zhang, D.-L.; Wei, Z.; Yu, L. *Sci. Bull.* **2017**, *62*, 1325.
(g) Tong, Q.; Gao, Q.; Xu, B.; Yu, L.; Fan, Y. *Chin. J. Org. Chem.* **2017**, *37*, 753 (in Chinese).
(仝庆, 高强, 许波连, 俞磊, 范以宁, 有机化学, **2017**, *37*, 753.)

[9] Rayman, M. *Lancet* **2012**, *379*, 1256.

[10] Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409.

[11] Cao, H.-E.; Zhu, B.-R.; Yang, Y.-F.; Xu, L.; Yu, L.; Xu, Q. *Chin. J. Catal.* **2018**, *39* 899.

[12] Yu, L.; Wang, J.; Chen, T.; Wang, Y.-G.; Xu, Q. *Appl. Organomet. Chem.* **2014**, *28*, 652.

[13] (a) Yu, L.; Qian, R.-R.; Deng, X.; Wang, F.; Xu, Q. *Sci. Bull.* **2018**, *63*, 1010.
(b) Zhang, H.; Han, M.-T.; Yang, C.-G.; Yu, L.; Xu, Q. *Chin. Chem. Lett.* **2019**, *30*, 263.

[14] Santoro, S.; Santi, C.; Sabatini, M.; Testaferri, L.; Tiecco, M. *Adv. Synth. Catal.* **2008**, *350*, 2881.

[15] Yu, L.; Wang, J.; Chen, T.; Ding, K.-H.; Pan, Y. *Chin. J. Org. Chem.* **2013**, *33*, 1096 (in Chinese).
(俞磊, 王俊, 陈天, 丁克鸿, 潘毅, 有机化学, **2013**, *33*, 1096.)
[16] Wang, Y.-G.; Yu, L.-H.; Zhu, B.-C.; Yu, L. *J. Mater. Chem. A* **2016**, *4*, 10828.
[17] Jing, X.; Yuan, D.; Yu, L. *Adv. Synth. Catal.* **2017**, *359*, 1194.
[18] (a) Yu, L.; Ye, J.-Q.; Zhang, X.; Ding, Y.-H.; Xu, Q. *Catal. Sci. Technol.* **2015**, *5*, 4830.
(b) Zhang, X.; Ye, J.; Yu, L.; Shi, X.; Zhang, M.; Xu, Q.; Lautens, M. *Adv. Synth. Catal.* **2015**, *357*, 955.
[19] (a) Deng, X.; Cao, H.-E.; Chen, C.; Zhou, H.-W.; Yu, L. *Sci. Bull.* **2019**, *64*, 1280.
(b) Deng, X.; Qian, R.; Zhou, W.; Yu, L. *Chin. Chem. Lett.* **2021**, doi: 10.1016/j.cclet.2020.09.012.
[20] Lee, C.-Y.; Kim, S.; Lee, K.-B.; Yoo, Y.-C.; Ryu, S.-Y.; Song, K.-S.; *Arch. Pharm. Res.* **2003**, *26*, 367.
[21] (a) Ribaudo, G.; Bellanda, M.; Menegazzo, I.; Wolters, L. P.; Bortoli, M.; Ferrer-Sueta, G.; Zagotto, G.; Orian, L. *Chem.-Eur. J.* **2017**, *23*, 2405.
(b) Goodman, M. A.; Detty, M. R. *Organometallics* **2004**, *23*, 3016.
[22] Ou, W.; Zou, R.; Han, M.-T.; Yu, L.; Su, C.-L. *Chin. Chem. Lett.* **2020**, *31*, 1899.
[23] Ribaudo, G.; Bellanda, M.; Menegazzo, I.; Wolters, L. P.; Bortoli, M.; Ferrer-Sueta, G.; Zagotto, G.; Orian, L. *Chem.-Eur. J.* **2017**, *23*, 2405.
[24] (a) Cao, H.; Qian, R.; Yu, L. *Catal. Sci. Technol.* **2020**, *10*, 3113.
(b) Liu, K.-J.; Deng, J.-H.; Yang, J.; Gong, S.-F.; Lin, Y.-W.; He, J.-Y.; Cao, Z.; He, W.-M. *Green Chem.* **2020**, *22*, 433.
(c) Xie, L.-Y.; Fang, T.-G.; Tan, J.-X.; Zhang, B.; Cao, Z.; Yang, L.-H.; He, W.-M. *Green Chem.* **2019**, *21*, 3858.
[25] (a) Nacca, F. G.; Monti, B.; Lenardão, E. J.; Evans, P.; Santi, C. *Molecules* **2020**, *25*, 2018.
(b) Peng, S.; Lin, Y.; He, W. *Chin. J. Org. Chem.* **2020**, *40*, 541 (in Chinese).
(彭莎, 林英武, 何卫民, 有机化学, **2020**, *40*, 541.)
(c) He, W.-B.; Gao, L.-Q.; Chen, X.-J.; Wu, Z.-L.; Huang, Y.; Cao, Z.; Xu, X.-H.; He, W.-M. *Chin. Chem. Lett.* **2020**, *31*, 1895.
(d) Xie, L.-Y.; Chen, Y.-L.; Qin, L.; Wen, Y.; Xie, J.-W.; Tan, J.-X.; Huang, Y.; Cao, Z.; He, W.-M. *Org. Chem. Front.* **2019**, *6*, 3950.

(Lu, Y.)

