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Short communication

Selenium-doped Fe_2O_3-catalyzed oxidative scission of C═C bond

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ABSTRACT

Selenium-doped Fe_2O_3 (Se@Fe_2O_3) was prepared by treating Fe_2O_3 with in situ generated NaHSe. The material was a low-cost but highly efficient and recyclable catalyst for oxidative scission of C═C. Compared with reported homogeneous $(RSe)_2$ catalyst (R = *c*-C_6H_{11}, $PhCH_2$, *n*-C_4H_9 etc), the turnover number of Se@Fe_2O_3 was enhanced (TON = 694 vs. 7) and the reaction did not require excess H_2O_2, affording a safer and more efficient method for alkene degradation under mild conditions.

1. Introduction

Catalytic oxidative scission of C═C is an important reaction not only for producing carbonyls, but also for the potentially comprehensive applications in degradation of large molecular including the biomass and organic pollutants [1–3]. However, the huge C═C bond energy brings a great challenge to achieve this objective. The existing technologies suffer from the use of expensive noble metal catalyst [4], some of which are hazardous to human beings and environments [5], solid waste-generation caused by the used chemical oxidants [6], harsh reaction conditions [7], high energy-consumption and tedious progresses [8]. Thus, developing easily accessible catalyst for oxidative scission of C═C under mild and green conditions is highly demanded. It is also a good basic theory research subject with profound application prospects, which continuously attracted our attention [9,10].

Yet, selenium (Se) has drawn much attention for its unique chemical- and bio-properties. Se-containing compounds have been extensively applied in organic synthesis [11–15], biochemistry [16], and materials science [17,18]. Se-containing compounds-catalyzed reactions are just unfolding [19–24], affording additional opportunities to develop novel green catalysis procedures with industrial application potential. Although Se-catalyzed oxidative scission of C═C bond has been reported by our group previously [25], the method required excess H_2O_2 oxidant and employed high-loading $(RSe)_2$ catalyst (R = *c*-C_6H_{11}, $PhCH_2$, *n*-C_4H_9 etc., 5 mol%), which, as a homogeneous catalyst, was unrecoverable and expensive for its tedious preparation progresses. Recently, combined with the works on nano catalysts [26–28], we developed Se-doped Fe_2O_3 (Se@Fe_2O_3) and it was found to possess very strong catalytic activity, allowing the oxidative C═C scission under mild conditions with no excess H_2O_2. Herein, we wish to report our findings.

2. Experimental

2.1. General experimental conditions

Chemicals and solvents were all purchased and used as received. All reactions were monitored Thin Layer Chromatography (TLC) with silica plate. Products were all purified by preparative TLC. Field emission scanning electron microscope (FE-SEM) images were determined on Zeiss_Supra55 instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance instrument (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR). Chemical shifts for ^1H NMR are relative to internal Me_4Si (0 ppm) and *J*-values are shown in Hz. The inductively coupled plasma-mass spectrometry (ICP-MS) analysis was performed on PerkinElmer Optima 7300 DV inductively coupled plasma spectrometer.

2.2. General procedures for the fabrication of Se@Fe_2O_3

1 mmol of Se powder (79.0 mg) and 1.5 mmol of $NaBH_4$ (56.7 mg) were sent into a round bottom flask charged with N_2. Under ice-water cooling, 3 mL of anhydrous EtOH was added into the flask and the mixture was kept at 0 °C for 4 h. 99 mmol of Fe_2O_3 (15.84 g) and 15 mL of anhydrous EtOH were added into the mixture, which was then stirred at room temperature for 12 h. After removing the solvent by distillation under reduced pressure with rotary evaporator, the residue was removed into a crucible and calcined in tube furnace at 550 °C for 5 h

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under N_2 protection. The obtained solid was grinded into powder before use.

2.3. General procedure for the Se@Fe_2O_3-catalyzed oxidative scission of C=C bond

1 mmol of alkene, Se@Fe_2O_3 catalyst and a piece of magnetic bar were added into a reaction tube. A solution of 30 *w*/w% H_2O_2 in 1 mL of solvent was then injected into the reaction tube and the obtained mixture was stirred and heated for 24 h. After evaporation of the solvent, the residue was subjected to preparative TLC to get the produced benzophenone. Specific substrate, catalyst amount, H_2O_2 amount, solvent and reaction temperature, were discussed in results and discussions section vide infra. Characterization data and ^{1}H and ^{13}C NMR spectra of products were given in supplementary data.

3. Results and discussions

Iron (Fe) is an abundant metal with extremely low cost for large-scale applications. Moreover, references have demonstrated that Fe could obviously enhance the catalytic activity of Se via a relay catalysis route so that air can be used as partial oxidant to reduce the used amount of H_2O_2 [29]. For these reasons, its oxide Fe_2O_3 was employed as the support of Se catalyst. Bearing electron-withdrawing oxygen, the Fe in Fe_2O_3 was electropositive to be attacked by HSe^-, which, as a strong nucleophile, was generated by reducing Se powder with $NaBH_4$ and was used in situ without separation [30]. Fig. 1 shows the approach for preparing Se@Fe_2O_3 catalyst and its micro-scale morphology in FE-SEM image, which illustrates a variety of loose nanostructures within 200 nm, allowing sufficient specific surface area for sufficient contact with the reactants.

The catalytic activity of Se@Fe_2O_3 for oxidative scission of C=C was then tested. Oxidation of ethene-1,1-diyldibenzene was chosen as the model reaction. Heating 1 mmol of ethene-1,1-diyldibenzene with 4 mmol of H_2O_2 (30 w/w%) in the presence of 30 mg of Se@Fe_2O_3 in 1,4-dioxane at 80 °C for 24 h, the desired oxidation product benzophenone could be separated in 26.9% yield. The H_2O_2 dosage was then examined and using H_2O_2/ethene-1,1-diyldibenzene at 2.0 mol/mol, which was the theoretical H_2O_2 amount for C=C scission to produce carbonyl, was screened out to be the preferable condition (Fig. 2a). The product yield decreased with insufficient or excess H_2O_2 amount. The former was caused by the incomplete conversion of the substrate, while in the latter reaction, a series of over-oxidation by-products, such as benzoic acid, phenol etc., were generated (as detected by GC–MS). Dosage of the Se@Fe_2O_3 catalyst was also examined (Fig. 2b). Using 40 mg of Se@Fe_2O_3 for the reaction of 1 mmol of ethene-1,1-diyldibenzene was favourable, leading to an elevated benzophenone yield at 40.2%, but further enhancing the catalyst amount resulted in a sharp decrease of product yield for elevated by-product generation.

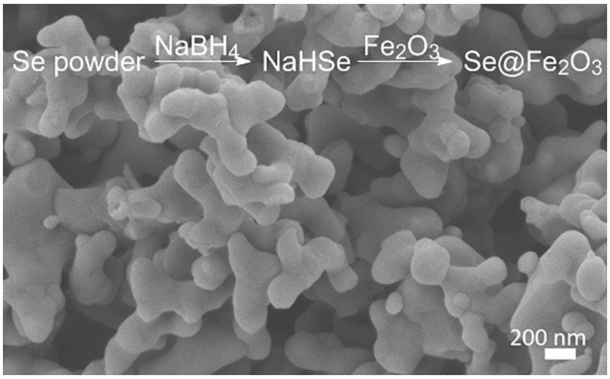


Fig. 1. Diagram for the synthesis of Se@Fe_2O_3 and its FE-SEM image.

A series of parallel experiments were performed to optimize the reaction conditions (Fig. 3). 80 °C, as initially employed, was the preferable reaction temperature. The reaction speed slowed down at low temperature, resulting in the incomplete conversion of ethene-1,1-diyldibenzene and the relevantly decreased benzophenone yield (Fig. 3a). Generation of over-oxidation by-products increased dramatically at the temperature over 90 °C (Fig. 3a). Besides 1,4-dioxane, toluene was also a favourable solvent for the reaction, giving benzophenone in 46.2% yield. EtOH, which was more environmental friendly, was also fit for the reaction to produce benzophenone in 42.3% yield. Unexpectedly, the use of EtOAc resulted in a sharp decrease of the product yield, while a series of unidentified by-products were generated and could be observed in TLC. DMC is an inflammable, green and cheap chemical in industrial production and it was found to be the most favourable solvent for the reaction among the candidates listed in Fig. 3b. Since ICP analysis showed that the Se@Fe_2O_3 catalyst contained ca 0.15 w/w% of Se, the TON of the reaction was calculated to be 694 on the basis of the involved Se amount. The used catalyst could be isolated from the reaction liquid by centrifugal separation and was reusable for the next turn of reaction without obvious deactivation (affording 50.3% product yield).

The substrate scope of the reaction was then examined. Besides ethene-1,1-diyldibenzene, the prop-1-en-2-ylbenzene substrate could afford the related product acetophenone in 67% yield. By introducing methyl as an electron donation group, 1-methyl-4-(prop-1-en-2-yl) benzene led to 1-(*p*-tolyl)ethan-1-one in elevated yield at 71%, while the electron-deficient substrate 1-chloro-4-(prop-1-en-2-yl)benzene afforded 1-(4-chlorophenyl)ethan-1-one in decreased yield at 53%. Trisubstituted ethene such as prop-1-ene-1,1-diyldibenzene led to the desired product benzophenone in 51% yield. For ethene-1,1,2-triyltribenzene bearing even larger steric hindrances, the benzophenone yield decreased to 42%. Oxidation of 1,1,2,2-tetraphenylethene did not occur under the Se@Fe_2O_3-catalyzed reaction conditions. The reactions of (*E*)-1,2-diphenylethene and styrene were also tested, and they led to benzoic acid in 72% and 78% yields respectively.

The mechanism of this interesting reaction was our next concern. First, a blank reaction with unselenized Fe_2O_3 as catalyst was performed under the standard conditions (see Section 2.3) and it produced benzophenone in only 19% yield, while a lot of the starting ethene-1,1-diyldibenzene was unconverted and could be recovered in 69% yield. This result demonstrated that doping Se was essential to act as an oxygen carrier catalyst for the transformation. Moreover, it has been attested by ^{77}Se NMR and X-ray photoelectron spectroscopy (XPS) analysis that oxidation of low-valent Se by H_2O_2 could produce the high-valent –SeO_3H (Eq. (1)) [31,32], which was highly active and participated the Se catalyzed oxidation reactions as an oxidative catalytic species. Since GC–MS analysis detected the existence of 2,2-diphenyloxirane, it was suggested that the reaction proceeded via an epoxidation step first.

Thus, on the basis of the experimental results as well as the references reports including our previous works on organoselenium catalysis [31–35], a plausible mechanism for this Se@Fe_2O_3-catalyzed oxidative cracking reaction was given below (Fig. 4). Epoxidation of the starting ethene-1,1-diyldibenzene initially afforded the intermediate 2,2-diphenyloxirane **A**. The hydration of **A** led to diol **B** [33], in which the proximal hydroxyl was even more active and could be oxidized into carboxyl of **C** in the presence of Se catalyst and H_2O_2 [34]. Further Se-catalyzed Baeyer-Villiger oxidation reaction of **C** led to the intermediate **D**, which produced the relatively stable benzophenone as the final product [35]. Notably, the reaction afforded benzophenone in 5.6% yield without H_2O_2 (Fig. 2a), showing that air might participate the reaction as a supplementary oxidant, so that no excess H_2O_2 was required.

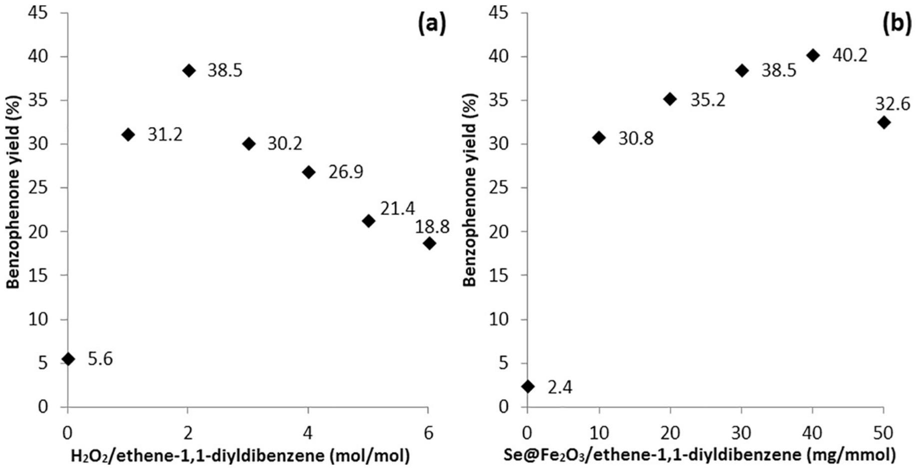


Fig. 2. Screenings of the dosage of H_2O_2 (a) and Se@Fe_2O_3 catalyst (b).

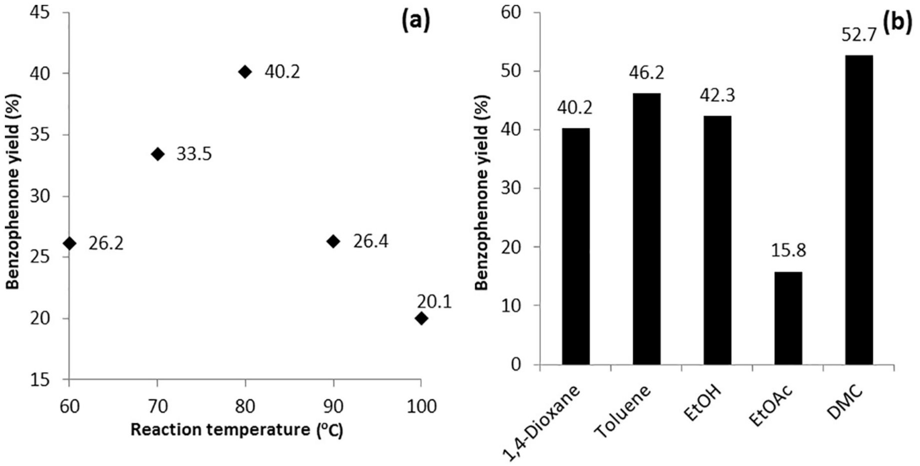
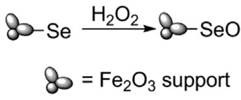


Fig. 3. Reaction conditions optimizations: (a) reaction temperature; (b) reaction solvent.



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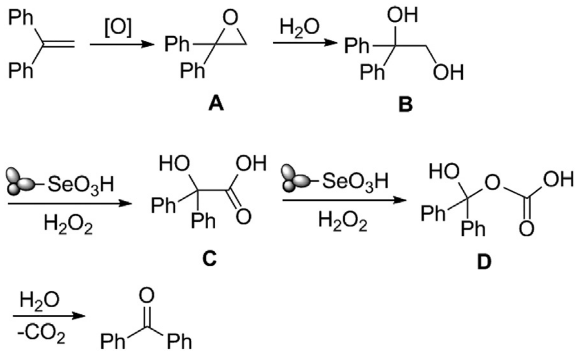

Fig. 4. Reaction mechanisms.

4. Conclusions

In conclusion, we found that, by doping Se into Fe_2O_3, the prepared Se@Fe_2O_3 possessed even higher catalytic activity than homogeneous $(RSe)_2$ catalyst (R = c-C_6H_{11}, $PhCH_2$, n-C_4H_9 etc) in the oxidative scission of C═C. In the reaction, the dosage of H_2O_2 was reduced, while the reactant was completely converted, affording an even safer and more efficient method for alkene degradation under mild conditions. Further investigations on the applications of this easily fabricated, low-cost and recyclable Se catalyst are ongoing in our laboratory.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105828.

References

[1] Y. Imada, Y. Okada, K. Noguchi, K. Chiba, Angew. Chem. Int. Ed. 58 (2019) 125–129.
[2] D. Pyszny, T. Piotrowski, B. Orlińska, Org. Process. Res. Dev. 23 (2019) 309–319.
[3] B.-T. Huang, J.-B. He, S.-Y. Bian, C.-J. Zhou, Z.-Y. Li, F.-N. Xi, J.-Y. Liu, X.-P. Dong, Chin. Chem. Lett. 29 (2018) 1698–1701.
[4] D. Xing, B.-T. Guan, G.-X. Cai, Z. Fang, L.-P. Yang, Z.-J. Shi, Org. Lett. 8 (2006) 693–696.

[5] K.C. Basavaraju, S. Sharma, R.A. Maurya, D.-P. Kim, Angew. Chem. Int. Ed. 52 (2013) 6735–6738.

[6] P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J.K. Bera, J. Am. Chem. Soc. 136 (2014) 13987–13990.

[7] A. Rubinstein, P. Jiménez-Lozanao, J.J. Carbó, J.M. Poblet, R. Neumann, J. Am. Chem. Soc. 136 (2014) 10941–10948.

[8] J.N. Moorthy, K.N. Parida, J. Org. Chem. 79 (2014) 11431–11439.

[9] L. Yu, R.-R. Qian, X. Deng, F. Wang, Q. Xu, Sci. Bull. 63 (2018) 1010–1016.

[10] H.-E. Cao, B.-R. Zhu, Y.-F. Yang, L. Xu, L. Yu, Q. Xu, Chin. J. Catal. 39 (2018) 899–907.

[11] T. Prochnow, A. Maroneze, D.F. Back, G. Zeni, J. Org. Chem. 84 (2019) 2891–2900.

[12] L.-H. Lu, Z. Wang, W. Xia, P. Cheng, B. Zhang, Z. Cao, W.-M. He, Chin. Chem. Lett. 30 (2019) 1237–1240.

[13] M.-X. Liu, Y.-M. Li, L. Yu, Q. Xu, X.-F. Jiang, Sci. China Chem. 61 (2018) 294–299.

[14] S. Kodama, T. Saeki, K. Mihara, S. Higashimae, S.-I. Kawaguchi, M. Sonoda, A. Nomoto, A. Ogawa, J. Org. Chem. 82 (2017) 12477–12484.

[15] A.A. Vieira, J.B. Azeredo, M. Godoi, C. Santi, E.N. da Silva Jr., A.L. Braga, J. Org. Chem. 80 (2015) 2120–2127.

[16] G.-M. Fang, X.-X. Chen, Q.-Q. Yang, L.-J. Zhu, N.-N. Li, H.-Z. Yu, X.-M. Meng, Chin. Chem. Lett. 29 (2018) 1033–1042.

[17] W.-M. Xu, K.-J. Chai, Y.-W. Jiang, J.-B. Mao, J. Wang, P.-F. Zhang, Y.-F. Shi, ACS Appl. Mater. Interfaces 11 (2019) 17670–17677.

[18] X. Jing, C. Chen, X. Deng, X. Zhang, D. Wei, L. Yu, Appl. Organomet. Chem. 32 (2018) e4332.

[19] F.V. Singh, T. Wirth, Catal. Sci. Technol. 9 (2019) 1073–1091.

[20] L. Yu, Huaxue Shiji 41 (2019) 545–549, https://doi.org/10.13822/j.cnki.hxsj.2019006844.

[21] Y. Zheng, A. Wu, Y. Ke, H. Cao, L. Yu, Chin. Chem. Lett. 30 (2019) 937–941.

[22] R. Guo, L. Liao, X. Zhao, Molecules 22 (2017) 835.

[23] A. Breder, S. Ortgies, Tetrahedron Lett. 56 (2015) 2843–2852.

[24] S. Santoro, J.B. Azeredo, V. Nascimento, L. Sancineto, A.L. Braga, C. Santi, RSC Adv. 4 (2014) 31521–31535.

[25] T.-T. Wang, X.-B. Jing, C. Chen, L. Yu, J. Org. Chem. 82 (2017) 9342–9349.

[26] S. Zhao, B. Xu, L. Yu, Y. Fan, Chin. Chem. Lett. 29 (2018) 884–886.

[27] S. Zhao, B. Xu, L. Yu, Y. Fan, Chin. Chem. Lett. 29 (2018) 475–478.

[28] D. Zhang, Z. Wei, L. Yu, Sci. Bull. 62 (2017) 1325–1330.

[29] C. Chen, X. Zhang, H. Cao, F. Wang, L. Yu, Q. Xu, Adv. Synth. Catal. 361 (2019) 603–610.

[30] S. Chu, H. Cao, T. Chen, Y. Shi, L. Yu, Catal. Commun. 129 (2019) 105730.

[31] Y. Wang, L. Yu, B. Zhu, L. Yu, J. Mater. Chem. A 4 (2016) 10828–10833.

[32] X. Jing, D. Yuan, L. Yu, Adv. Synth. Catal. 359 (2017) 1194–1201.

[33] L. Yu, J. Wang, T. Chen, K.-H. Ding, Y. Pan, Chin. J. Org. Chem. 33 (2013) 1096–1099.

[34] K. Cao, X. Deng, T. Chen, Q. Zhang, L. Yu, J. Mater. Chem. A 7 (2019) 10918–10923.

[35] H.-E. Cao, M.-X. Liu, R.-R. Qian, X. Zhang, L. Yu, Appl. Organomet. Chem. 33 (2019) e4599.