DE GRUYTER
Green Processing and Synthesis 2021; 10: 677–686

Research Article

Jingjing Sun, Qianqian Zhu, Xiaoyan Guo*, Haibo Jin*, Guangxiang He, Lei Ma, Rongyue Zhang, Qingyang Gu, and Suohe Yang

Baeyer–Villiger co-oxidation of cyclohexanone with Fe–Sn–O catalysts in an O_2/benzaldehyde system

https://doi.org/10.1515/gps-2021-0045
received January 14, 2021; accepted June 24, 2021

Abstract: Baeyer–Villiger (BV) oxidation of cyclohexanone to ε-caprolactone was studied by a co-precipitation method using Fe–Sn–O catalysts in an O_2/benzaldehyde system. The effects of the Fe:Sn ratio, calcination temperature, calcination time, and reaction conditions on the catalytic performance were investigated. The catalysts present the best activity when it is prepared at a Fe:Sn ratio of 1:1, calcination temperature of 850°C, and calcination time of 5 h. Under these conditions, catalysts form a large number of small prisms, which result in a larger specific surface area and enhanced catalytic activity. The optimum reaction conditions for the synthesis of ε-caprolactone in the presence of the Fe–Sn–O catalyst are as follows: catalyst (0.12 g), 1,2-dichloroethane (30 mL), O_2 flow rate of $25\,\mathrm{mL\,min^{-1}}$, cyclohexanone to benzophenone of 3:1, reaction temperature of 60°C, and reaction time of 5 h. The conversion of cyclohexanone and the average yield of ε-caprolactone are determined at 98.96% and 83.36%, respectively.

Keywords: BV oxidation, ε-caprolactone, oxidation of cyclohexanone, Fe–Sn–O catalyst

1 Introduction

ε-Caprolactone is a new type of polyester monomer that has been utilized in a variety of applications. It is predominantly used in the synthesis of poly-ε-caprolactone or modification by blending or copolymerization with other esters [1,2]. The key methods for the synthesis of ε-caprolactone include oxidation of cyclohexanone by the Baeyer–Villiger (BV) reaction, intramolecular condensation of 6-hydroxycaproic acid, catalytic dehydrogenation of 1,6-hexanediol, and diester hydrogenation of hexamethylene glycol. Particularly, the BV oxidation of cyclohexanone is the most widely employed approach [3]. BV oxidation is a very important reaction in the organic synthesis for designing value-added lactone/esters from the respective carbonyl compounds. Usually an active metal-containing material catalyzes this reaction in the presence of peroxides [4–6]. According to the utilized raw materials, BV oxidation of cyclohexanone can include H_2O_2, O_2/air, peroxyacid, or biological oxidation.

Currently, ε-caprolactone is mainly prepared by the peroxyacid oxidation method [7,8]. The approach is widely used in the industry to produce ε-caprolactone using organic peroxic acids, such as peroxyformic [9], peracetic [10], peroxybenzoic [11], 3-chloroperoxybenzoic [12], and trifluoro-peracetic acids [13]. Nevertheless, organic peroxy acids are expensive and are associated with certain risks, particularly during the purification and concentration processes. In addition, acidic waste is a serious environmental pollutant. Recycling carboxylic acids and separation of byproducts in the later stages of the synthesis is challenging.

In contrast, bio-oxidation approaches utilize the high specificity and efficiency of enzymes. Such methods are more environmentally friendly and can be conducted under relatively mild reaction conditions. However, enzymes exhibit poor stability, and the production cost is high. Moreover, bio-oxidation is associated with significant environmental requirements and risks. Furthermore, the method

---

*** Corresponding author: Xiaoyan Guo,** Department of Chemical Engineering, Beijing Institute of Petrochemical and Technology, Beijing Key Laboratory of Fuels Cleaning and Advanced Catalytic Emission Reduction Technology, Beijing 102617, China, e-mail: guoxiaoyan@bipt.edu.cn
*** Corresponding author: Haibo Jin,** Department of Chemical Engineering, Beijing Institute of Petrochemical and Technology, Beijing Key Laboratory of Fuels Cleaning and Advanced Catalytic Emission Reduction Technology, Beijing 102617, China, e-mail: jinhaibo@bipt.edu.cn
Jingjing Sun, Qianqian Zhu, Guangxiang He, Lei Ma, Rongyue Zhang, Qingyang Gu, Suohe Yang: Department of Chemical Engineering, Beijing Institute of Petrochemical and Technology, Beijing Key Laboratory of Fuels Cleaning and Advanced Catalytic Emission Reduction Technology, Beijing 102617, China

involving H_2O_2 oxidation uses low concentration H_2O_2 as the oxidant, and the main by-product is water. Nonetheless, to improve the performance, the use of a catalyst displaying high activity is required. Commonly employed catalysts include Lewis acids, metal ion-loaded polymers, and metal oxides. Due to the low polarity of cyclohexanone, the addition of an organic solvent is typically necessary. Unfortunately, organic solvents can participate in the reaction mixture and co-oxidize with H_2O_2.

The O_2/air oxidation method appears to be the most optimal; however, it has been conducted only on a laboratory scale [14]. O_2 is a relatively clean oxidant; therefore, utilizing it for the oxidation of cyclohexanone to ε-caprolactone would be environmentally friendly, economical, and safe. An approach involving O_2/air oxidation would also generate fewer by-products. Similar to H_2O_2, O_2 is not a sufficiently strong oxidant; hence, the addition of a co-oxidant would be necessary for the effective oxidation of cyclohexanone. Zhou et al. [15] demonstrated that the catalytic activity of iron tetraphenylporphyrin (Fe-TCPP) in the synthesis of ε-caprolactone by the O_2/air oxidation method was better than that of Ru, Co, and Mn phenyl porphyrin catalysts. In addition, Belaroui et al. [16] reported loading iron phthalocyanine (Fe-Phtal) on SiO_2 to obtain a Fe-Phtal/SiO_2 catalyst, which was employed in the O_2/air oxidation of cyclohexanone to ε-caprolactone, affording the product in a 61% yield. Jeong et al. [17] prepared a Fe-TCPP-PMO catalyst by loading Fe-TCPP on organo-energetic mesoporous silica. The generated catalyst displayed higher activity in the O_2/air oxidation than pure Fe-TCPP. Numerous other catalysts, including those loaded on molecular sieves, transition metal-based materials, metal oxides, non-metal oxides (e.g., graphene) [18], Cu-MCM-41 [19,20], SnO_2, and CuO [21,22], have been reported. Among them, benzaldehyde is the most frequently used catalyst [23–25].

During the reaction, O_2 first oxidizes benzaldehyde to benzoic acid, which subsequently oxidizes cyclohexanone to ε-caprolactone. However, as mentioned earlier, the oxidation ability of O_2 is weak; thus, the use of highly active metal oxide or composite metal oxide catalysts is essential. Specifically, catalysts containing Fe and Sn metals are often used in this process [17,26–29]. In the present study, we prepared an Fe-Sn composite metal oxide catalysts [30–32], referred to as Fe–Sn–O, which is used to catalyze the synthesis of ε-caprolactone in the presence of a O_2/benzaldehyde system. The effects of different calcination temperatures, calcination times, and metal ratios on the performance of the catalyst are investigated. A feasible green synthesis method for the preparation of ε-caprolactone is proposed.

2 Experimental

2.1 Preparation of the Fe–Sn–O catalyst

A 5% solution of Na_2CO_3 was added to a three-necked flask and heated at 60°C. A total of $0.15\,\mathrm{mol\,L^{-1}}$ $Fe(NO_3)_3\cdot 9H_2O$ and $0.15\,\mathrm{mol\,L^{-1}}$ $SnCl_4\cdot 5H_2O$ precursor solutions were added dropwise to the flask with stirring [33,34]. Then, $2\,\mathrm{mol\,L^{-1}}$ NaOH was then used to adjust the pH to 10. The reaction mixture was stirred for 2 h and then placed in an electrically heated blast drying oven set to 60°C for 48 h. The reaction mixture was washed with deionized water until pH 7. Subsequently, the co-precipitate was dried in an electrically heated blast drying oven at 100°C for 24 h, crushed, and calcined in a muffle furnace at a heating rate of $5\,°\mathrm{C\,min^{-1}}$ up to a certain temperature for a specific amount of time. After cooling the calcined product to room temperature, metal oxide particles of 40–60 mesh were sieved to obtain the Fe–Sn–O catalyst.

2.2 BV co-oxidation reaction of cyclohexanone

The BV reaction was carried out in a 100 mL three-necked flask. Briefly, 0.15 g of the catalyst and 35 mL of 1,2-dichloroethane were added to the flask in the presence of oxygen at a flow rate controlled at $20\,\mathrm{mL\,min^{-1}}$. After 15 min, 0.01 mol cyclohexanone and 0.04 mol benzaldehyde were added sequentially. The reaction mixture was heated to 55°C and stirred for 5 h. The reaction mixture was then cooled for 1 h and the catalyst was separated by filtration.

GC-2014C (SHIMADZU, Japan) was equipped with an FID detector. The temperature program mode (120°C for 3 min, $10\,°\mathrm{C\,min^{-1}}$ to 240°C for 15 min) was used to analyze the extracted reaction solution. The chromatographic column was HP-5 50 m × 0.200 mm. N_2 was used as carrier gas at the nitrogen pressure of 0.5 MPa. The detector temperature was 260°C, and injection port temperature was 260°C. The injection quantity was 0.3 μL.

2.3 Characterization of the Fe–Sn–O catalyst

Figure 1 illustrates the X-ray diffraction (XRD) spectra of Fe–Sn–O prepared at different calcination temperatures.

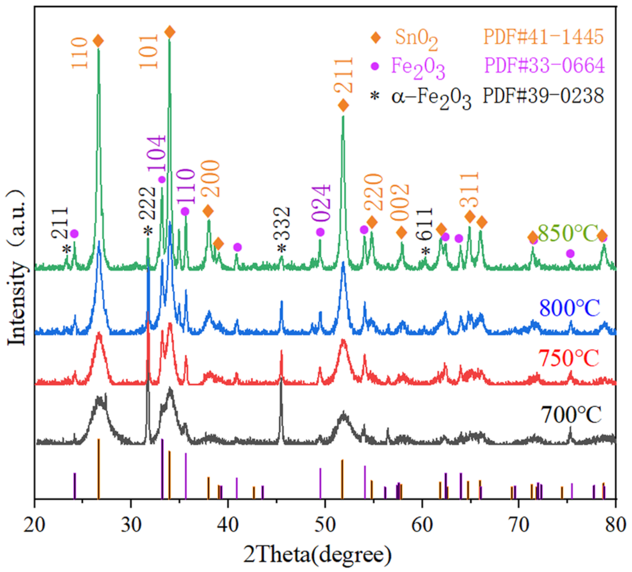

Figure 1: XRD spectrum of the Fe–Sn–O catalyst at different calcination temperatures of 700°C, 750°C, 800°C, and 850°C.

The spectrum of the Fe–Sn–O catalyst exhibits three characteristic peaks (i.e., $2\theta = 26.693°$, $33.960°$, and $51.860°$), which are consistent with the (110), (101), and (211) crystal planes of SnO_2 (PDF#41-1445), respectively. In addition, the peaks at $2\theta = 33.160°$, $35.621°$, and $54.120°$ are consistent with the crystal planes of Fe_2O_3 (PDF#33-0664), and the peaks at $2\theta = 32.976°$, $45.186°$, and $60.176°$ are consistent with the crystal planes of α-Fe_2O_3 (PDF#39-0238). Hence, the catalyst is a composite metal oxide composed of Fe_2O_3 and SnO_2. Notably, the higher the calcination temperature, the stronger the characteristic diffraction peaks and the better the crystallinity.

Figure 2 shows the scanning electron microscopy (SEM) images of the Fe–Sn–O catalyst at different calcination temperatures. From Figure 2, at a calcination temperature of 700°C, Fe–Sn–O is a sparse and porous agglomerate formed by the accumulation of smaller particles. Furthermore, at a calcination temperature of 750°C, the surface particles begin to grow, and the surface of the agglomerates becomes smooth. When the calcination temperature reached 800°C, the surface particles grow into small prisms, which are less obvious. The catalyst is formed by the accumulation of these small prismatic particles. The appearance of prismatic particles on the surface is detected at a calcination temperature of 850°C. A detailed qualitative inspection of nanostructured materials is obtained from the TEM and HRTEM images shown in Figure 3. In Figure 3a, it can be seen that the distribution of nanoparticles in the sample is the same as the SEM result. The Fe–Sn–O catalyst is

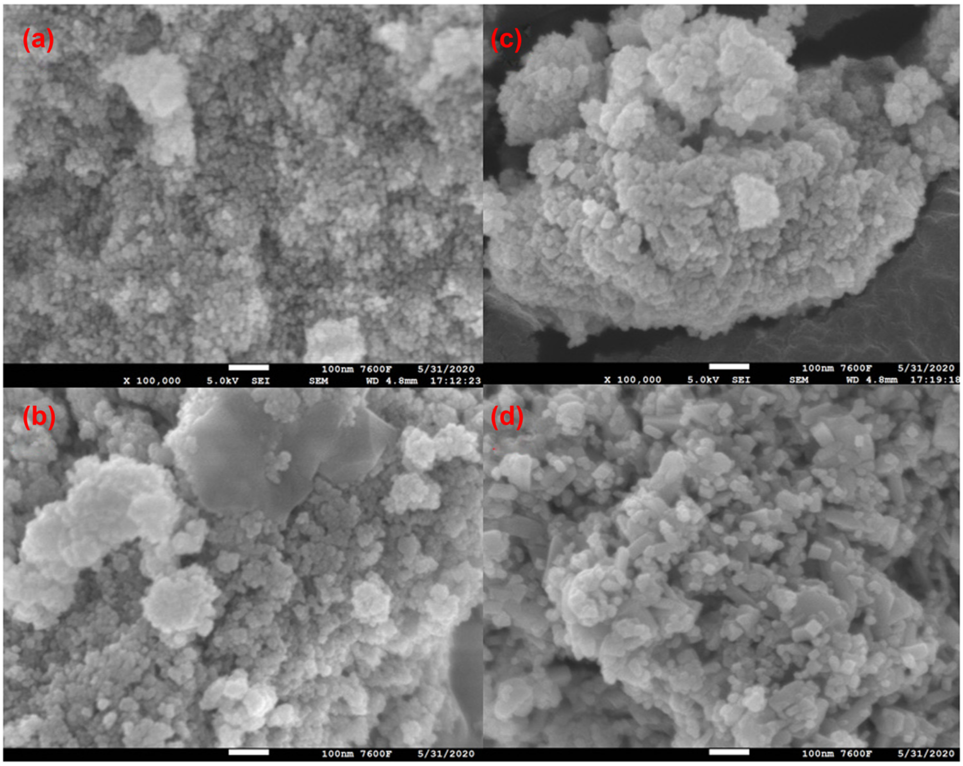

Figure 2: SEM images of the Fe–Sn–O catalyst at different calcination temperatures of (a) 700°C, (b) 750°C, (c) 800°C, and (d) 850°C.

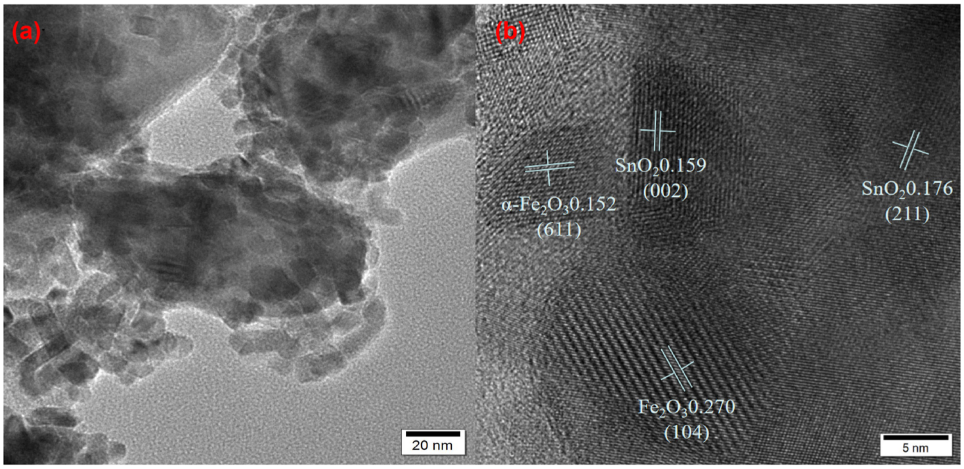

Figure 3: TEM image (a) and HRTEM image (b) of Fe–Sn–O catalyst calcined at 850°C.

composed of prismatic particles at a calcination temperature of 850°C. In Figure 3b, some lattice fringes can be observed, in which the grain boundary spacing d = 0.159 nm and d = 0.176 nm are attributed to the (002) and (211) crystal planes of SnO_2, respectively, which is the same as 57.818° and 51.780° in XRD. The peaks coincide with each other; the grain boundary spacing d = 0.152 nm and d = 0.270 nm are attributed to the (611) crystal plane of α-Fe_2O_3 and the (104) crystal plane of Fe_2O_3, respectively, which are consistent with the peaks at 60.676° and 33.152° in XRD. All in all, Fe–Sn–O catalyst shows the best activity when calcined at 850°C. This is due to the accumulation of prismatic particles, resulting in a sparser structure than in the case of smooth particles. Consequently, the Fe–Sn–O catalyst displays a larger specific surface area and pore volume, leading to enhanced activity.

Figure 4a illustrates the Fourier transform infrared (FTIR) spectra of the Fe–Sn–O catalyst at different calcination temperatures. The broad absorption peak at ~3,460 cm^{-1} corresponds to the O–H bond of the hydroxyl molecules on the surface of Fe–Sn–O or the stretching vibration of water molecules adsorb on the surface of the catalyst. The absorption peak attributed to the vibration of the Fe–O bond is detected in the fingerprint region at ~500 cm^{-1}. Finally, the absorption peak between ~1,500 and 1,700 cm^{-1} is ascribed to the vibration of the Sn–O bond.

Figure 4b demonstrates the H_2 temperature-programmed reduction (TPR) diagrams of the Fe–Sn–O catalysts prepared at different calcination temperatures. In the figure, the peak at around 710°C corresponds to reduction of Sn^{4+} to Sn, while that at 520°C indicates the reduction of Fe_2O_3. Moreover, the reduction temperature is higher during calcination at 800°C and 850°C.

Based on the Brunauer–Emmett–Teller (BET) analysis, the specific surface area of the Fe–Sn–O catalyst is found to decrease with the increasing calcination temperature (see Table 1). Fe–Sn–O also displays the better activity at this temperature range. Moreover, the increase in the calcination temperature leads to the agglomeration of crystal grains on the surface of the catalyst. This results in a smaller specific surface area, which is consistent with the SEM evaluation. In addition, as the calcination temperature increases, the pore volume and pore diameter increase, which makes it easier for reactants and products with larger molecular diameters to enter and leave the catalyst. This is also an important reason for the stronger catalyst activity at this calcination temperature.

3 Results and discussion

3.1 The Fe–Sn–O preparation conditions

3.1.1 Effect of the metal ratio on the catalytic performance of Fe–Sn–O

The metal ratio in the composite metal oxide has a significant effect on the reaction. The Fe–Sn–O catalysts exhibiting Fe:Sn ratios of 0.5:1, 1:1, 1.5:1, and 2:1 are prepared by calcination at 600°C for 4 h.

As it can be seen in Figure 5, when the n(Fe):n(Sn) ratio is increased from 0.5:1 to 1:1, the cyclohexanone conversion rate and the yield of ε-caprolactone slightly increase. In contrast, the conversion rate and yield decrease with the increase of Sn in the Fe–Sn–O catalyst.

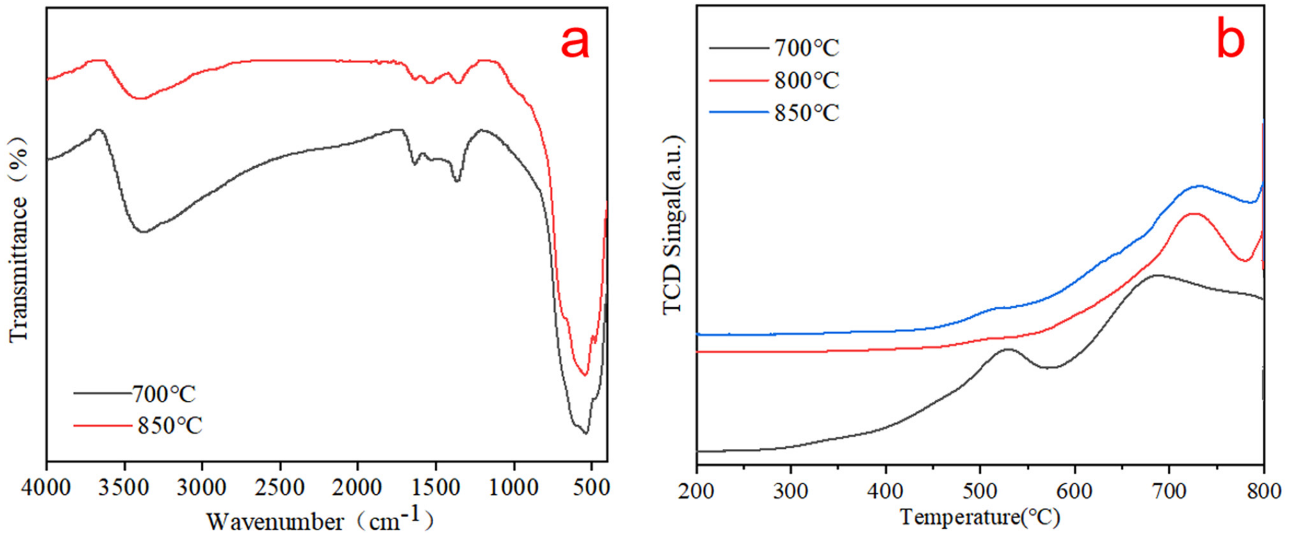

Figure 4: FTIR spectra (a) and H_2-TPR diagram (b) of the Fe–Sn–O catalyst prepared at different calcination temperatures.

Table 1: Specific surface area, pore volume, and pore size distribution of the Fe–Sn–O catalyst at different calcination temperatures

Calcination temperature (°C)	700	750	800	850
Specific surface area ($m^2\,g^{-1}$)	35.352	35.102	16.152	13.387
Pore volume ($mL\,g^{-1}$)	0.062	0.054	0.046	0.087
Pore size (nm)	5.568	5.689	7.452	9.635

Generally, Fe is a key for the improvement of the reaction conversion rate, while Sn plays a role in enhancing the selectivity. Thus, finding the most optimal Fe:Sn ratio is essential to achieve high yields. In addition, the phases and structures of the catalysts exhibiting different metal ratios might also affect their activity. In the present, the most suitable metal ratio is established to be *n*(Fe):*n*(Sn) = 1:1.

3.1.2 Effect of the calcination temperature on the catalytic performance of Fe–Sn–O

The catalyst calcination temperature also affects its structure, leading to varying activity. Different Fe–Sn–O catalysts are prepared by calcination at 700°C, 750°C, 800°C, and 850°C for 4 h at the *n*(Fe):*n*(Sn) ratio of 1:1. The activities of the resulting catalysts are evaluated.

As it can be seen in Figure 6, an increase in the calcination temperature to 850°C results in increases in both the cyclohexanone conversion rate and the ε-caprolactone yield. As the temperature continues to increase, the conversion rate and yield decrease. This is because the Fe_2O_3 and SnO_2 pores generated at a low calcination temperature are not sufficiently developed. In addition, the specific surface area and volume of the catalyst are not large enough, which results in poor catalytic activity, low cyclohexanone conversion rate, and low ε-caprolactone yield. When the calcination is conducted at 900°C, the activity of the catalyst begins to decrease. Hence, 850°C is the most suitable catalyst calcination temperature.

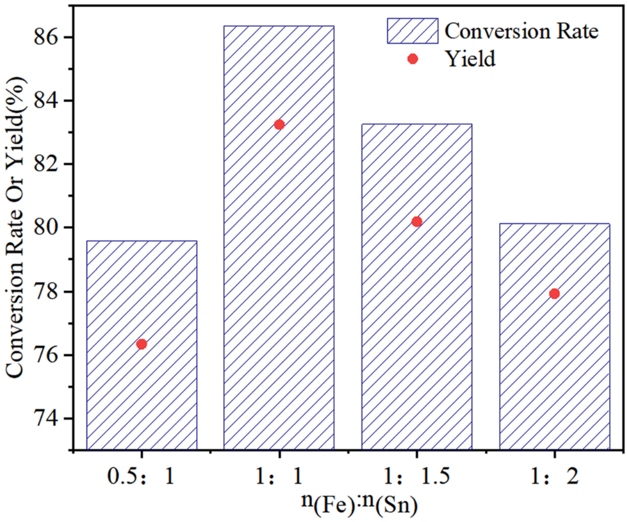

Figure 5: Effect of the metal ratio on the catalytic performance of Fe–Sn–O.

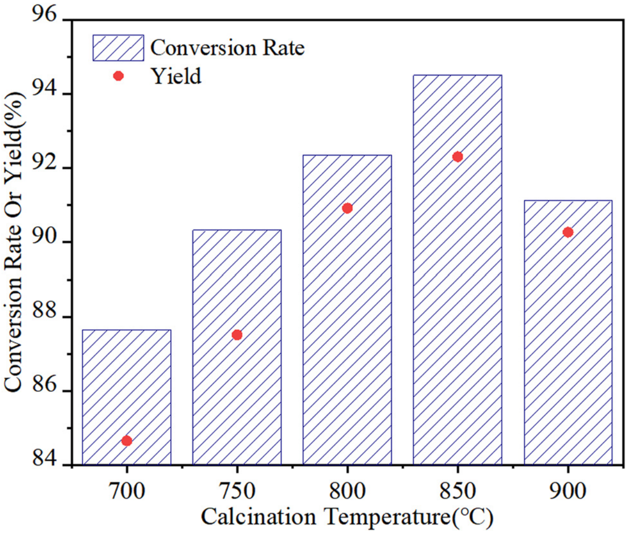

Figure 6: Effect of the calcination temperature on the catalytic performance of Fe–Sn–O.

3.1.3 Effect of calcination time on the catalytic performance of the Fe–Sn–O catalyst

The Fe–Sn–O catalyst is calcined for 2, 3, 4, and 5 h at a *n*(Fe):*n*(Sn) ratio of 1:1 and calcination temperature of 850°C. The effect of the calcination time on the catalytic performance of the Fe–Sn–O catalyst is investigated.

As shown in Figure 7, when the calcination time is less than 5 h, the activity of the Fe–Sn–O catalyst increases with an increase of the calcination time. In contrast, when the calcination time is more than 5 h, the activity of the catalyst remains nearly unchanged. This is because the $Fe(OH)_3$ and $Sn(OH)_4$ species in the precursor are only partially decomposed at short calcination times, resulting in lower catalyst activity. The metal hydrates completely decompose into metal oxides after 5 h of calcination. Under these conditions, the activity of the catalyst is the highest. When the catalyst calcination time is further increased, the metal oxide and catalyst activity remain unchanged. Hence, the most suitable calcination time is 5 h.

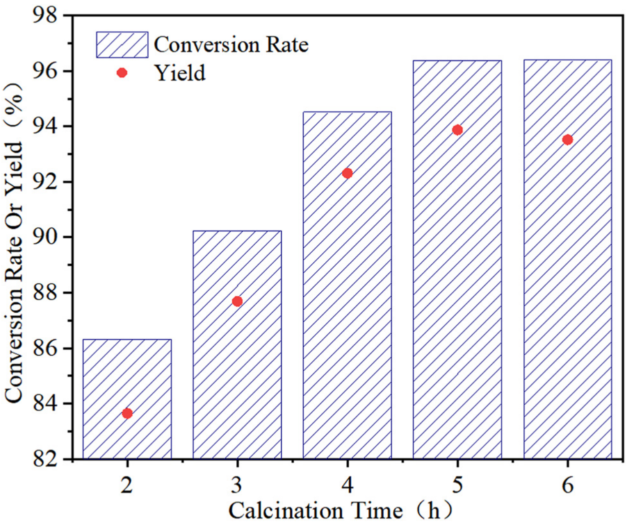

Figure 7: Effect of the calcination time on the catalytic performance of Fe–Sn–O.

3.2 Benzaldehyde oxidation reaction conditions

3.2.1 Effect of the O_2 amount on the reaction

The amount of oxidant used in the investigated reaction is a key factor affecting its outcome. As it can be seen in Figure 8, the cyclohexanone conversion rate and ε-caprolactone yield initially increase with the increase of the oxygen flow rate. When the flow rate is over 25 mL min^{-1}, the reaction performance reaches a maximum. According to Henry's law, when the temperature and pressure are constant, the solubility of O_2 in the reaction solution is also constant. Thus, when the flow rate is continuously increased, the concentration of O_2 in the reaction solution remains unchanged. Correspondingly, the cyclohexanone conversion rate and ε-caprolactone yield keep constant during the reaction. Hence, the optimal O_2 flow rate is 25 mL min^{-1}.

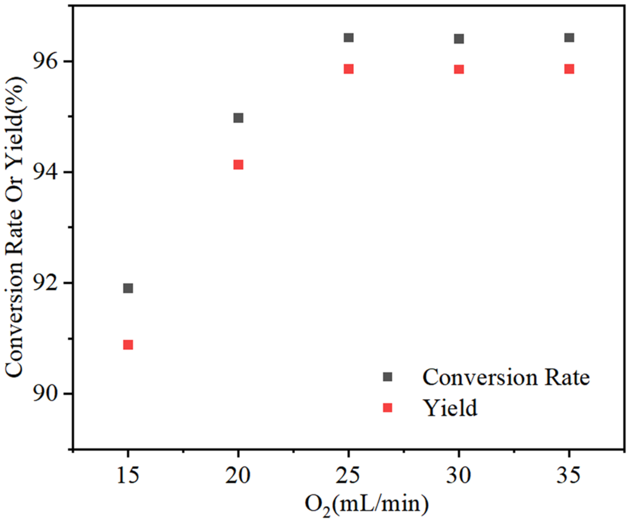

Figure 8: Effect of the O_2 amount on the ε-caprolactone yield. Reaction conditions: cyclohexanone (0.02 mol), benzaldehyde (0.06 mol), 1,2-dichloroethane (30 mL), Fe–Sn–O (0.12 g), 55°C, 5 h.

3.2.2 Effect of the amount of benzaldehyde on the reaction

During the reaction, benzaldehyde participates and acts as a co-oxidant to oxidize cyclohexanone in the presence of O_2. Thus, its amount in the reaction also affects the cyclohexanone conversion rate and ε-caprolactone yield (see Figure 9). From Figure 9, the cyclohexanone conversion rate and ε-caprolactone yield initially increase with the increase of $n_{\text{(cyclohexanone)}}$:$n_{\text{(benzaldehyde)}}$ and then slowly decrease. The most optimal ratio of $n_{\text{(cyclohexanone)}}$:$n_{\text{(benzaldehyde)}}$ is established to be 1:3. Under these conditions, the cyclohexanone conversion rate and ε-caprolactone yield are 96.43% and 95.87%, respectively. This is because the concentration of the cyclohexanone substrate in the reaction is constant. When excess benzaldehyde is used, the substrate concentration decreases, leading to a decrease in the reaction rate.

3.2.3 Effect of the reaction temperature

According to Henry's law, high temperatures reduce the solubility of gases in the solution of reaction, which can affect its reaction performance. Moreover, the temperature also has an effect on the number of activated molecules in the reaction. From Figure 10, the cyclohexanone conversion rate and ε-caprolactone yield initially increase with the increase of the temperature and reach the highest values at 60°C (98.97% conversion and 98.34% yield, respectively). Conversely, the cyclohexanone conversion rate and ε-caprolactone yield decrease at the reaction temperature of 65°C. This is attributed to the reduced solubility of O_2 in the reaction solution due to the high reaction temperature. Thus, the optimal reaction temperature is determined to be 60°C.

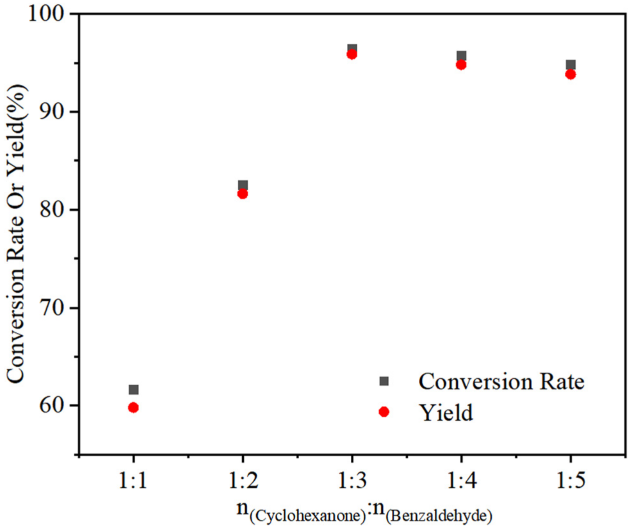

Figure 9: The effect of the amount of benzaldehyde on the ε-caprolactone yield. Reaction conditions: cyclohexanone (0.02 mol), 1,2-dichloroethane (30 mL), Fe–Sn–O (0.12 g), O_2 (20 mL min^{-1}), 55°C, 5 h.

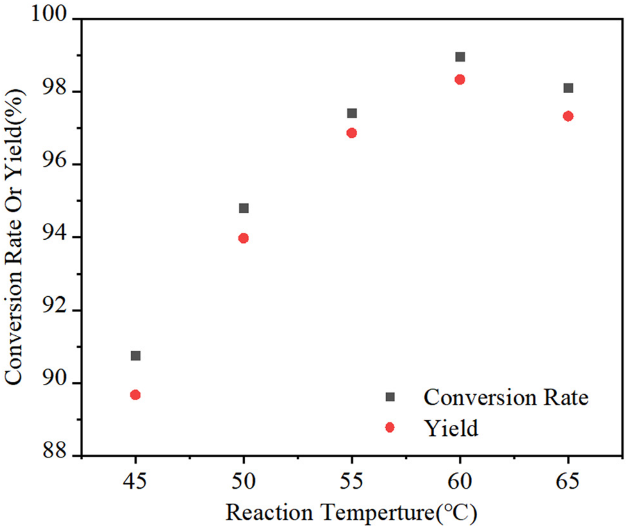

Figure 10: Effect of the reaction temperature on the ε-caprolactone yield. Reaction conditions: cyclohexanone (0.02 mol), benzaldehyde (0.06 mol), 1,2-dichloroethane (30 mL), Fe–Sn–O (0.12 g), O_2 (20 mL min^{-1}), 5 h.

3.2.4 Effect of the reaction time on the reaction

As shown in Figure 11, the cyclohexanone conversion rate and ε-caprolactone yield initially increase with the reaction time and reach a maximum of 98.97% and 98.34%, respectively, at 5 h. Furthermore, it is found that the conversion rate and yield started to gradually decrease after 5 h. This is because the amount of cyclohexanone in the reaction continued to decrease as the reaction progressed until reaching equilibrium at 5 h. Hence, the optimal reaction time is 5 h.

3.2.5 Investigation of the reaction stability

Using the optimized reaction conditions, specifically Fe–Sn–O catalyst (0.12 g), 1,2-dichloroethane (30 mL), O_2 (25 mL min^{-1} flow rate), $n_{\text{(cyclohexanone)}}$:$n_{\text{(benzaldehyde)}}$ ratio of 3:1, reaction temperature of 60°C, and reaction time of 5 h, three parallel experiments are used to

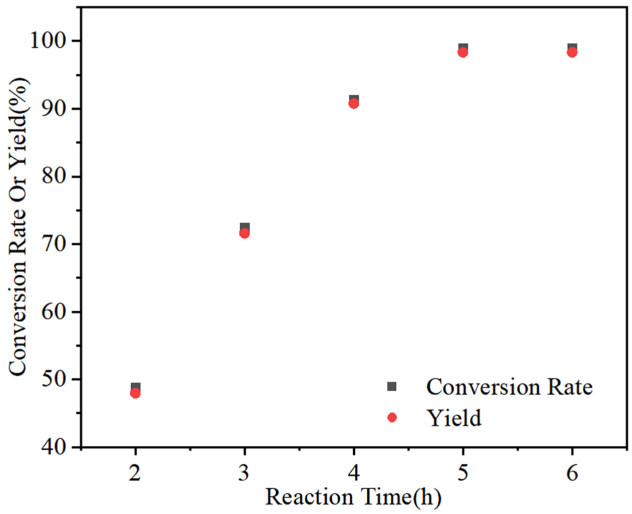

Figure 11: Effect of the reaction time on the *ε*-caprolactone yield. Reaction conditions: cyclohexanone (0.02 mol), benzaldehyde (0.06 mol), 1,2-dichloroethane (30 mL), Fe–Sn–O (0.12 g), O_2 (20 mL min^{-1}), 60°C.

investigate the reaction stability. The results are obtained in Table 2.

4 Conclusion

In the present study, we prepared a Fe–Sn–O composite catalyst by a co-precipitation method using $Fe(NO_3)_3·9H_2O$ and $SnCl_4·5H_2O$ as the precursors and Na_2CO_3 as the co-precipitation agent. The reaction conditions are investigated in detail, and the obtained Fe–Sn–O catalysts are characterized by XRD, SEM, BET, FTIR, and H_2-TPR analyses. The effects of the structural characteristics and surface morphology on the catalytic performance of the synthesized material are evaluated. The catalyst is used to catalyze a BV oxidation of cyclohexanone to *ε*-caprolactone in the presence of an O_2/benzaldehyde system. We examined the reaction conditions such as the amount of the Fe–Sn–O catalyst, O_2, and benzaldehyde as well as the reaction temperature and time. It is found that the catalyst exhibits the best activity at a Fe:Sn ratio of 1:1, calcination temperature of 850°C, and calcination time of 5 h. Under these conditions, the surface of the Fe–Sn–O catalyst appears as an accumulation of small prisms, which results in a large specific surface area and pore volume. The BET analysis demonstrates that the maximum specific surface area is 207.813 $m^2\ g^{-1}$, while the maximum pore size is 0.193 nm. In addition, the XRD evaluation reveals the best crystallinity of the material at a calcination temperature of 850°C. The optimal reaction conditions are as follows: Fe–Sn–O catalyst (0.12 g), 1,2-dichloroethane (30 mL), O_2 (25 mL min^{-1}), $n_{(cyclohexanone)}:n_{(benzaldehyde)} = 3:1$, reaction temperature of 60°C, and reaction time of 5 h. Under these conditions, the average cyclohexanone conversion rate reaches 98.96%, whereas the average *ε*-caprolactone yield is established at 98.36%. Hence, in the current work, we achieved oxidation of cyclohexanone to *ε*-caprolactone using a BV oxidation reaction under mild conditions. Importantly, the described method is inexpensive and environmentally friendly.

Table 2: Investigation of the reaction stability

Serial number	Cyclohexanone conversion rate (%)	Yield of *ε*-caprolactone (%)
1	98.95	98.33
2	98.96	98.35
3	98.98	98.39
Average	98.96	98.36

Funding information: Financial supported by the National Natural Science Foundation of China (91634101) and The Project of Construction of Innovative Teams and Teacher Career Development for Universities and Colleges under Beijing Municipality (IDHT20180508).

Author contributions: Jingjing Sun: writing – original draft, writing – review and editing, methodology, and formal analysis; Qianqian Zhu: writing – original draft, formal analysis, andconceptualization; Xiaoyan Guo: writing – review and editing, formal analysis, and investigation; Haibo Jin: writing – review and editing, resources, and funding acquisition; Guangxiang He: resources and methodology; Lei Ma: supervision; Rongyue Zhang: validation; Qingyang Gu: formal analysis; Suohe Yang: software.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Reference

[1] Shinzaburo O. Studies on lactone formation in vapor phase. II. Synthesis of *ε*-caprolactone. B Chem Soc Jpn. 1962;35(4):562–6. doi: 10.1246/bcsj.35.562.

[2] Mckay AF, Tarlton EJ, Petri SI, Steyermmark PR, Mosley MA. Amino acids. V. 1,3-Di-(ι-carboxyalkyl)-thioureas and their chemistry. J Am Chem Soc. 1958;80(6):1510–7. doi: 10.1021/ja01539a058.

[3] Lu QS, Xiao Y, Xie HH, Huang CM, Li Y, Yao XS. Progress in the production process of ε-caprolactone. Mod Chem Ind. 2015;35(2):42–5. doi: org/10.1002/ceat.202070065.

[4] Asim B, Prashant K, Rajiv K. Baeyer-Villiger rearrangement catalyzed by titanium silicate molecular sieve (TS-1)/H_2O_2 system. Catal Lett. 1996;40(1–2):47–50. doi: 10.1007/BF00807456.

[5] Manidipa P, Nabanita P, John M, Manickam S, Asim B. New mesoporous magnesium–aluminum mixed oxide and its catalytic activity in liquid phase Baeyer-Villiger oxidation reaction. Chem Eng Sci. 2012;71:564–72. doi: 10.1016/j.ces.2011.11.038.

[6] Sumbul R, Nagasuresh E, Ruth G, Asim B, Debasis S, Mazumdar S, et al. Aerobic Baeyer–Villiger oxidation of cyclic ketones over periodic mesoporous silica Cu/Fe/Ni/Co-HMS-X. Appl Catal A-gen. 2015;505:515–23. doi: 10.1016/j.apcata.2015.03.014.

[7] Baj S, Chrobok A, Siewniak A. New and efficient technique for the synthesis of ε-caprolactone using $KHSO_5$ as an oxidising agent in the presence of a phase transfer catalyst. Appl Catal A-gen. 2011;395(1–2):49–52. doi: 10.1016/j.apcata.2011.01.022.

[8] Zhu QQ, Jin HB, Guo XY, He GX, Ma L, Zhuang RY, et al. Study on synthesis of ε-caprolactone with MgO catalysis by Baeyer-Villiger green oxidation of cyclohexanone in H_2O_2/acetonitrile system. Ciesc J. 2021;72(5):2638–46. doi: 10.11949/0438-1157.20201245.

[9] Lambert A, Elings JA, Macquarrie JD, Carr G, Clark HJ. The Baeyer-Villiger oxidation of ketones using HMS supported peroxycarboxylic acids. Synlett. 2000;7:1052–4. doi: 10.1055/s-2000-6666.

[10] Koo DH, Kim M, Chang S. WO_3 Nanoparticles on MCM-48 as a highly selective and versatile heterogeneous catalyst for the oxidation of olefins, sulfides, and cyclic ketones. Org Lett. 2005;22(7):5015–8. doi: 10.1021/ol052019i.

[11] Luo WP, Yan MQ, Tao B, Shi SL, Chen B. Solubility of succinic acid, glutaric acid and adipic acid in propionic acid + ε-caprolactone + water mixtures: Experimental measurement and thermodynamic modeling. J Chem Thermodyn. 2019;138:332–44. doi: 10.1016/j.jct.2019.06.033.

[12] Kotsuki H, Arimura K, Araki T, Shinohara T. Sc(OTf)$_3$- and TfOH-catalyzed Baeyer-Villiger oxidation of carbonyl compounds with m-chloroperbenzoic acid. Synlett. 1999;4:462–4. doi: 10.1055/s-1999-2648.

[13] Choudary BM, Sridhar C, Sateesh M, Sreedhar B. Microencapsulated bismuth(III) triflate catalyst for organic transformations. J Mol Catal A: Chem. 2004;212(1/2):237–43. doi: 10.1016/j.molcata.2003.10.037.

[14] Li Y. Catalytic oxidation of the epsilon-caprolactone for the synthesis of cyclohexanone. China: Wuhan University of Technology; 2017.

[15] Zhou XT, Ji HB, Yuan QL. Baeyer-Villiger oxidation of ketones catalyzed by iron(III) meso-tetraphenyl porphyrin chloride in the presence of molecular oxygen. J Porphyr Phthalocyanines. 2018;12(2):94–100. doi: 10.1142/S1088424608000121.

[16] Belaroui LS, Sorokin AB, Figueras F, Bengueddach A, Milletet MJ. Comparative Baeyer-Villiger oxidation of cyclohexanone on Fe-pillared clays and iron tetrasulfophthalocyanine covalently supported on silica. Cr Chim. 2010;13(4):466–72. doi: 10.1016/j.crci.2010.01.007.

[17] Jeong EY, Ansari MB, Park SE. Aerobic Baeyer–Villiger oxidation of cyclic ketones over metalloporphyrins bridged periodic mesoporous organosilica. ACS Catal. 2011;1(8):855–63. doi: 10.1021/cs200163r.

[18] Zheng C, Chang S, Yang C, Lian D, Ma C, Zhang C, et al. Enhanced shape selective catalysis of mixed cyclic ketones in aerobic Baeyer-Villiger oxidation with magnetic Cu-Fe_3O_4 supported mesoporous silica microspheres. Tetrahedron. 2011;74(21):2608–16. doi: 10.1016/j.tet.2018.04.009.

[19] Zhou Z, Wang J, Qin J, Yu Y, Wu WL. The multifunctional mesoporous Sn-Cu-Ti catalysts for the B-V oxidation of cyclohexanone by molecular oxygen. J Porous Mat. 2018;25(3):835–43. doi: 10.1007/s10934-017-0496-9.

[20] Ma Y, Liang Z, Feng S, Zhang Y. Baeyer–Villiger oxidation of cyclohexanone by molecular oxygen with Fe–Sn–O mixed oxides as catalysts. Appl Organomet Chem. 2015;29(7):450–5. doi: 10.1002/aoc.3314.

[21] Zhang XY, Yang HL, Yang GX, Li SW, Wang X, Ma JT. Metal-free mesoporous SiO_2 nanorods as a highly efficient catalyst for the Baeyer-Villiger oxidation under mild conditions. ACS Sustain Chem Eng. 2018;6(5):5868–76. doi: 10.1021/acssuschemeng.7b04167.

[22] Li YF, Guo MQ, Yin SF, Chen L, Zhou YB, Qiu RH, et al. Graphite as a highly efficient and stable catalyst for the production of lactones. Carbon. 2013;55(2):269–75. doi: 10.1016/j.carbon.2012.12.036.

[23] Subramanian H, Koodali RT. Baeyer-Villiger oxidation of cyclic ketones over iron-containing mesoporous MCM-48 silica materials. React Kinet Catal L. 2008;95(2):239–45. doi: 10.1007/s11144-008-5352-0.

[24] Kawabata T, Ohishi Y, Itsuki S, Fujisaki N, Shishido T, Takaki K, et al. Iron-containing MCM-41 catalysts for Baeyer–Villiger oxidation of ketones using molecular oxygen and benzaldehyde. J Mol Catal A-Chem. 2005;236(1–2):99–106. doi: 10.1016/j.molcata.2005.03.027.

[25] Zang J, Ding JY, Li Y, Wang T, Li Y, Gong LF. Highly efficient and reusable Cu-MCM-41 catalyst for the Baeyer–Villiger oxidation of cyclohexanone. Catal Commun. 2014;51:24–8. doi: 10.1016/j.catcom.2014.03.022.

[26] Chen SY, Zhou X, Li Y, Luo RC, Ji HB. Biomimetic Baeyer-Villiger oxidation of ketones with SnO_2 as cocatalyst, features in activating carbonyl group of substrates. Chem Eng J. 2014;241:138–44. doi: 10.1016/j.cej.2013.12.027.

[27] Chen SY, Zhou TX, Ji HB. Insight into the cocatalyst effect of 4A molecular sieve on Sn(II) porphyrin-catalyzed BV oxidation of cyclohexanone. Catal Today. 2015;264:191–7. doi: 10.1016/j.cattod.2015.07.051.

[28] Zhou Z, Wang J, Qin J, Yu Y, Wu WL. The multifunctional mesoporous Sn–Cu–Ti catalysts for the BV oxidation of cyclohexanone by molecular oxygen. J Porous Mat. 2018;25(3):835–43. doi: 10.1007/s10934-017-0496-9.

[29] Huo H, Wu L, Ma J, Yang HL, Zhang L, Yang YY, et al. Fabrication of Fe_3O_4-l-dopa-Cu^{II}/Sn^{IV}@ Micro-Mesoporous-SiO_2 catalyst applied to Baeyer-Villiger oxidation reaction. ChemCatChem. 2016;8(4):779–86. doi: 10.1002/cctc.201501107.

[30] Carballeira JD, Alvarez E, Sinisterra JV. Biotransformation of cyclohexanone using immobilized Geotrichum candidum NCYC49: factors affecting the selectivity of the process.

J Mol Catal B-enzym. 2004;28(1):25–32. doi: 10.1016/j.molcatb.2004.01.009.

[31] Bornadel A, Hatti-Kaul R, Hollmann F, Kara S. A Bi-enzymatic convergent cascade for ε-caprolactone synthesis employing 1,6-hexanediol as a 'Double-Smart Cosubstrate'. ChemCatChem. 2015;7(16):2442–5. doi: 10.1002/cctc.201500511.

[32] Romero E, Rubén GC, Mattevi A, Fraaije MW. Characterization and crystal structure of a robust cyclohexanone monooxygenase. Angew Chem Int Ed. 2016;55(51):15852–5. doi: 10.1002/ange.201608951.

[33] Yang Z, Niu L, Ma Z, Ma HC, Lei ZQ. Fabrication of highly active Sn/W mixed transition-metal oxides as solid acid catalysts. Transit Met Chem. 2011;36(3):269–74. doi: 10.1007/s11243-011-9465-3.

[34] Zhang GX, Ren XC, Zhang HB, Yu P, Gui SY. $MgO/SnO_2/WO_3$ as catalysts for synthesis of ε-caprolactone over oxidation of cyclohexanone with peracetic acid. Catal Commun. 2015;58:59–63. doi: 10.1016/j.catcom.2014.08.031.