

Catalytic conversion of glycerol to formic acid under mild condition over an iron-based catalytic system

Robby Sudarman^{1*}, *Carolus Borromeus Rasrendra*², and *Tatang Hernas Soerawidjaja*²

¹Chemical Engineering Department, Bandung State Polytechnic, 40559 Bandung Barat, Indonesia

²Chemical Engineering Department, Bandung Institute of Technology, 40132 Bandung, Indonesia

Abstract. Glycerol, produced in large amounts as the main by-product of biodiesel production from biomass, has great potential to be converted into formic acid which is a potential hydrogen carrier. This research aims to evaluate the performance of an iron-based catalytic system in the oxidation process of glycerol to formic acid. The methods used include preparing an iron (II) oxalate catalyst, determining the reaction medium and reaction time for glycerol oxidation, optimizing the conditions of the glycerol oxidation process, and analysing the glycerol oxidation products. Optimization of process conditions includes the influence of temperature, substrate/catalyst molar ratio, and oxidant/substrate molar ratio. The research showed that water was a better reaction medium for glycerol oxidation, with a reaction time of 240 minutes. Oxidation of glycerol with an iron (II) oxalate catalyst can produce formic acid products with the best results obtained at pH 5, temperature 50°C, substrate/catalyst molar ratio of 100, and oxidant/substrate molar ratio of four with 83.18% converted glycerol. The yield and selectivity of formic acid were 47.77% and 57.43% respectively. These results indicate that the iron-based catalytic system has the potential to be an effective catalytic system for glycerol oxidation under mild conditions.

1 Introduction

Formic acid (H_2CO_2) is the simplest carboxylic acid and a commodity chemical widely used in the industrial world, such as the chemical, textile, leather, pharmaceutical, rubber, and other industries [1, 2]. Formic acid can also be used as a direct energy source in direct formic acid fuel cell/DFAFC technology [3]. The most exciting use of formic acid currently is as a promising hydrogen storage compound [4]. Formic acid can be decomposed into hydrogen (H_2) in a fast and selective process under mild conditions through a reaction system with a metal catalyst [5, 6]. The possibility of formic acid as a hydrogen carrier is economically and ecologically meaningful only when renewable feedstock and low-cost processes are used for formic acid production [7].

* Corresponding author: robby.sudarman@polban.ac.id

So far, formic acid is produced conventionally from unsustainable fossil-based raw materials [8], so an alternative production of formic acid from sustainable biomass-based raw materials is needed. Glycerol derived from biomass is very interesting to propose as a raw material for formic acid production because it is abundant as a by-product during biodiesel production via transesterification [9, 10]. The presence of primary and secondary alcohol groups in the glycerol molecule makes it reactive and promising as a feedstock for the sustainable production of formic acid [11, 12].

The conversion of glycerol to formic acid has been carried out through a glycerol oxidation reaction mechanism using various catalysts. Interest in using iron-based catalysts as substitutes for rare and more expensive transition metals in organic synthesis reactions is increasing [13]. This is due to the need to implement more sustainable reactions following the principles of green chemistry, where iron, which is abundant and relatively non-toxic, is currently considered a metal with minimum safety concerns [14].

Studies on using iron-based catalysts in oxidation reactions have long been known. It has been reported that iron complexes can powerfully catalyze alcohol oxidation reactions either by molecular oxygen or hydrogen peroxide [15, 16]. Crotti and Farnetti [17] specifically studied the oxidation of glycerol by hydrogen peroxide using a complex catalyst of iron (II) trifluoromethane sulfonate ($\text{Fe}(\text{OTf})_2$), and they could produce formic acid with selectivity of 98% but with a conversion that was still below 50%. This is an exciting challenge to produce formic acid with high conversion and selectivity using an iron-based catalyst. Thus, this study proposes a robust iron-based catalytic system utilizing catalytic material that is economically cheaper but has an excellent catalytic performance. A simple Iron (II)-based metal-organic framework, iron (II) oxalate, is utilized in this study due to its known significant oxidation activity in degrading organic compounds through the Fenton reaction [18].

Ramirez et al. [19] found that the iron (II) oxalate catalyst showed great catalytic activity in the orange II oxidation process with a decomposition of up to 99%. Additionally, Zhang et al. [9] found that oxalic acid indirectly increased formic acid production from glycerol oxidation because it played a role in preventing further formic acid oxidation. Based on these past results, the oxalate ligand is considered suitable for controlling the iron atom to become an active and selective catalysis site in the oxidation process. This research aims to assess the performance of iron (II) oxalate as catalyst in glycerol oxidation to produce formic acid.

2 Material and method

Hydrogen peroxide is used as an oxidant for the Fenton reaction in the glycerol oxidation process with iron (II) oxalate catalytic system. The oxidation reaction was carried out in a three-neck flask reactor using standard reflux techniques.

2.1 Materials

The materials used in this study include materials for the synthesis of catalysts which include distilled water, ferrous ammonium sulphate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$), oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), and sulfuric acid (H_2SO_4). The materials for glycerol oxidation include glycerol, hydrogen peroxide (H_2O_2), acetone (CH_3COCH_3), distilled water (H_2O), and sodium hydroxide (NaOH).

2.2 Preparation of iron catalyst

The iron (II) oxalate catalyst was prepared by simple dissolution of ferrous ammonium sulphate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$) powder in oxalic acid [20]. Iron (II) oxalate was precipitated as a yellow powder.

2.3 Determination of reaction time and medium

A mixture of acetone/water with a volume ratio of 2:1 as solvent was tested and compared with water solvent as a reaction medium for the glycerol oxidation process. Reaction time plays a vital role in the chemical reaction process, so glycerol oxidation for four and six hours was investigated in this study.

2.4 Optimization of process conditions

In this research, the influence of several process variables on glycerol oxidation was investigated so that suitable operating process conditions could be obtained. The benchmark for the success of the glycerol oxidation process is measured based on the glycerol conversion value and the yield and selectivity of formic acid obtained. Process conditions were optimized by investigating the influence of several process variables, including reaction temperature, substrate/catalyst molar ratio, and oxidant/substrate molar ratio.

2.5 Analysis of oxidation products

The liquid product from glycerol oxidation was analysed qualitatively and quantitatively using an HPLC instrument equipped with an RID detector using an HPX-87H column. Sulfuric acid with a concentration of 0.005 M was used as the mobile phase with a flow rate of 0.6 mL/minute at 60°C. The work curve of each compound detected is first plotted using the pure chemical compound in question to obtain a standard curve, which is then used to determine the percentage of unreacted glycerol and formic acid products obtained. Furthermore, the moles of glycerol and formic acid products can be calculated and used in calculating glycerol conversion and formic acid yield and selectivity as follows.

$$\text{Conversion (\%)} = \frac{(\text{moles of glycerol charged} - \text{moles of glycerol left})}{\text{moles of glycerol charged}} \times 100 \quad (1)$$

$$\text{H}_2\text{CO}_2 \text{ Yield (\%)} = \frac{\text{moles of formic acid}}{3 \times \text{moles of glycerol charged}} \times 100 \quad (2)$$

3 Result and discussion

The result and discussion in this study are described as follows.

3.1 Determination of glycerol oxidation reaction medium

In this study, we first investigated the effect of the reaction medium because the catalytic reaction performance is dependent on the medium, as shown in the research by Crotti and Farnetti [17], who found that their catalytic system is suitable with a mixture of acetonitrile/water as a medium. In this study, the performance of the iron-based catalytic system using water and acetone/water mixture with a volume ratio of 2:1 as a reaction medium was investigated. Acetone was chosen as the solvent in this study because it can

dissolve hydrophilic compounds such as glycerol, miscibility with polar and non-polar solvents, and moderately low toxicity [21].

In this initial experiment, hydrogen peroxide (H_2O_2) was used as an oxidant for glycerol oxidation with experimental conditions: glycerol/Fe molar ratio of 100, pH 5, room temperature, and reaction time of 240 minutes. The response to the results of the glycerol oxidation reaction in the form of conversion, yield, and selectivity of formic acid (H_2CO_2) is shown in Figure 1.

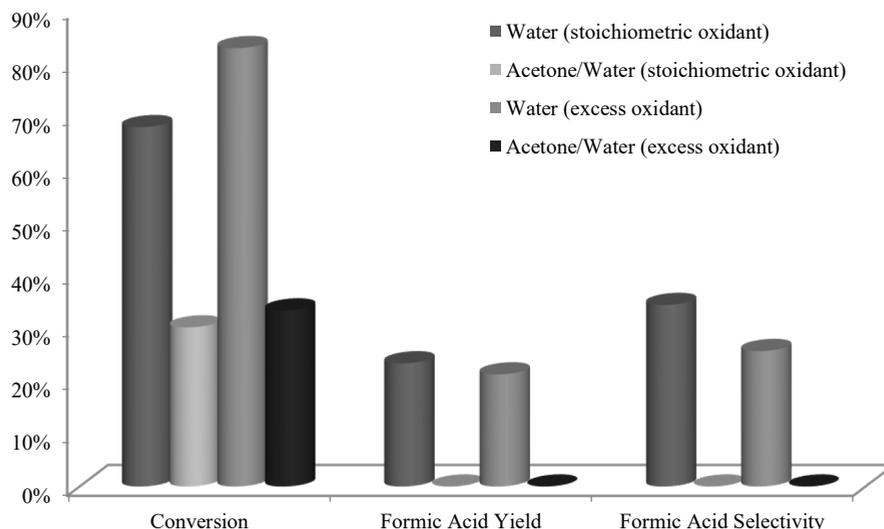


Fig. 1. Effect of reaction medium on glycerol conversion and formic acid's yield and selectivity.

The iron (II) oxalate catalyst can catalyse the glycerol oxidation reaction using either water or acetone/water mixture as the reaction medium. However, the glycerol oxidation reaction using water went better than a mixture of acetone/water as a reaction medium. This is shown in Figure 1, where the glycerol oxidation reaction using an acetone/water mixture as a reaction medium has a minor conversion than water, namely 30.09% and 67.87%, respectively. Glycerol was not converted to formic acid but became another product in experiments using an acetone/water mixture as the reaction medium. This can be caused by acetone, which can also be oxidized by hydrogen peroxide, disrupting the glycerol oxidation reaction.

Based on the results of this experiment, it is known that the reaction medium greatly influences the glycerol oxidation reaction, and it is found that water is the appropriate reaction medium for glycerol oxidation with iron (II) oxalate catalyst. Water as a reaction medium plays a good role in the oxidation of glycerol due to the nature of water, which can dissolve the reactants (glycerol feed, H_2O_2 oxidant, and iron (II) oxalate catalyst) well so that collisions between reactant molecules to carry out chemical reactions can take place well. Moreover, the employment of water, which is an environmentally friendly solvent, is the fundamental principle of green chemistry [22]. Glycerol has limited solubility, as stated by Crotti and Farnetti [17], so there are no further tests with another solvent.

3.2 Determination of glycerol oxidation reaction time

Reaction time plays a vital role in the chemical reaction process because sufficient reaction time determines the amount of feed converted and the product produced. Therefore, experiments were carried out to determine the appropriate reaction time for the glycerol oxidation process, which produces formic acid under experimental conditions: pH 5, glycerol/Fe molar ratio of 100, H₂O₂/glycerol molar ratio of 4, and ambient temperature. The response to the results of the glycerol oxidation reaction in the form of conversion, yield, and selectivity for formic acid (H₂CO₂) is presented in Figure 2.

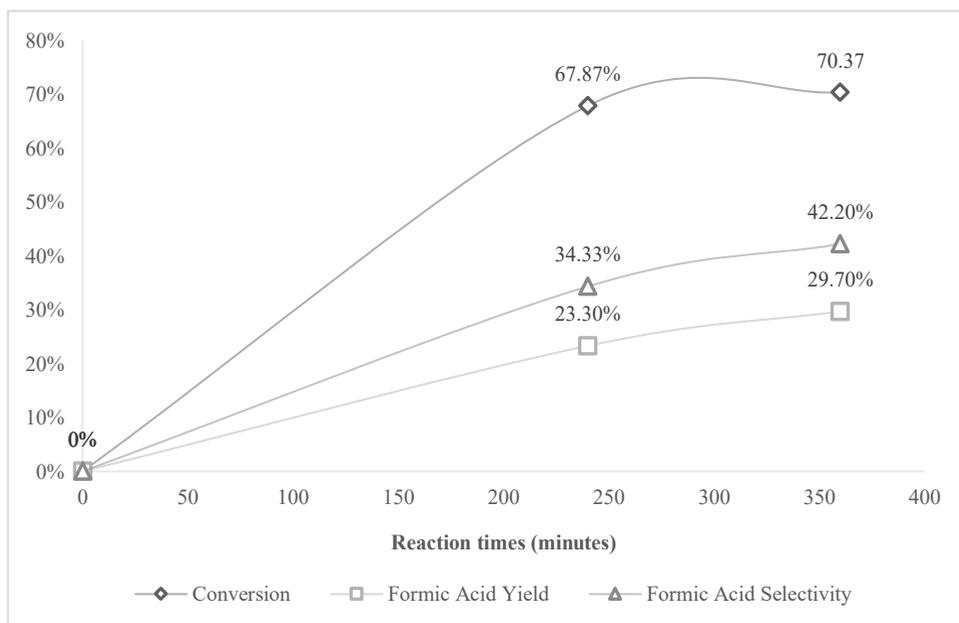


Fig. 2. Effect of reaction time on glycerol conversion and formic acid's yield and selectivity.

Based on the experimental results, the longer the reaction time, the less glycerol feed. This shows that the conversion increased with increasing reaction time, as shown in Figure 2. Glycerol converted by 67.87% at a reaction time of 240 minutes increased to 70.37% at a reaction time of 360 minutes. Apart from that, the yield and selectivity of formic acid also increased along with increasing reaction time. The increase in the amount of glycerol feed that is converted into the product as the reaction time increases is caused by the increasing number of reactant molecules (glycerol, H₂O₂ oxidant, and iron (II) oxalate catalyst) colliding with each other to carry out the chemical reaction. Based on the experimental results, it is known that the increase in glycerol conversion is not significant in the time interval from 240 minutes to 360 minutes, namely only increasing by 2.5%.

3.3 Optimization of Experimental Conditions for the Oxidation of Glycerol to Formic Acid

Optimization of experimental conditions in the glycerol oxidation process was carried out to obtain feasible operating process conditions and to maximize the formation of the desired formic acid product. In this experiment, the oxidation process was carried out using a catalysis system prepared from 0.1 mmol of iron (II) oxalate with water as the reaction medium and H₂O₂ as the oxidant for 240 minutes. The experimental condition parameters investigated include the substrate/catalyst molar ratio, oxidant/substrate molar ratio, initial

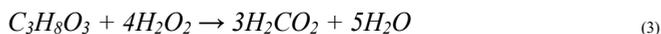
pH of the solution, and reaction temperature. Responses in the form of conversion, yield, and selectivity of formic acid are presented in Table 1.

Table 1. Glycerol oxidation under various experimental conditions.

T (°C)	H ₂ O ₂ /Glycerol	Glycerol/Fe	Initial pH	Final pH	Conversion	FA Yield	FA Selectivity
25	4	100	5	2	67.87%	23.30%	34.33%
25	4	1000	5	2	14.39%	0%	0%
25	6	100	5	3	82.75%	21.20%	25.62%
25	6	1000	5	3	17.90%	0%	0%
25	4	100	3	2	67.75%	22.50%	33.22%
25	4	100	10	10	30.23%	0%	0%
25	6	100	3	2	100.00%	30.53%	30.53%
25	6	100	10	5	32.65%	0%	0%
50	4	100	5	2	83.18%	47.77%	57.43%
50	4	100	3	3	81.69%	31.15%	38.14%
90	4	100	3	2	94.10%	42.35%	45.01%

Based on the experimental results in Table 1, the substrate/catalyst molar ratio significantly influences the glycerol conversion and the resulting formic acid yield (Table 1 numbers 1, 2, 3, and 4). Under the condition that the glycerol/Fe molar ratio of 100, the glycerol conversion was 67.87%, and the formic acid yield was 23.30%. When the glycerol/Fe molar ratio was increased tenfold to 1000, the glycerol conversion decreased to 14.39%, and formic acid was not formed under this condition. Glycerol conversion only slightly increased to 17.90% when the amount of oxidant was increased beyond the stoichiometric amount under this condition. This is because, at a substantial glycerol/Fe molar ratio, the amount of catalyst is much smaller than that of glycerol substrate to be converted, so it is insufficient for the glycerol oxidation process. This phenomenon shows that the iron catalyst must have enough to oxidize glycerol. Based on the experimental results, the molar ratio of glycerol/Fe of 100, or in other words, the percentage of iron catalyst to the glycerol substrate of 1%, is the appropriate amount for the oxidation process of glycerol to formic acid.

In this experiment, the amount of oxidant H₂O₂ had an essential influence on the glycerol oxidation reaction with an iron catalyst, as Crotti and Farnetti [17] reported. The effect of the amount of oxidant was observed based on variations in the H₂O₂/glycerol molar ratio, which was determined based on the reaction equation for the oxidation of glycerol with the oxidant H₂O₂ (Equation 3).



One mole of glycerol requires four moles of H₂O₂ to be converted into three moles of formic acid so that stoichiometrically, an H₂O₂/glycerol molar ratio of four is required. As for excess oxidant conditions, the reaction is carried out with a molar ratio of H₂O₂/glycerol of six. An increase in the H₂O₂/glycerol molar ratio causes the amount of converted glycerol to increase, as shown in Table 1 (numbers 1 and 3). Initially 67.87%, the glycerol conversion increased to 82.75% when excess oxidant was used.

At a lower pH, namely pH 3, glycerol conversion increased significantly from 67.75% to 100% as the H₂O₂/glycerol molar ratio increased (Table 1, numbers 5 and 7). At pH 3, the yield of formic acid increases along with the increase in the H₂O₂/glycerol molar ratio,

namely from 22.50% to 30.53%. Meanwhile, at a higher pH, namely at pH 10, an increase in the H_2O_2 /glycerol molar ratio only causes a slight increase in glycerol conversion from 30.23% to 32.65% (Table 1 numbers 6 and 8). At this pH, formic acid is not formed at the end of the reaction.

In acidic solutions, the iron (II) oxalate catalyst shows good catalytic activity in the oxidation process of glycerol to formic acid due to the low pH (2-4) being favourable for the classic Fenton reaction carried out with a homogeneous Fe (II) catalyst which can soluble [23]. This is shown by the conversion value, which reaches 100% when excess H_2O_2 oxidant is used at pH 3. Therefore, acidic conditions with pH 3 are the best in the glycerol oxidation process with an iron (II) oxalate catalyst at room temperature. This follows research by Ramirez et al. [19], who found the best results for the degradation of Orange II using an iron (II) oxalate catalyst at pH 3. Meanwhile, under alkaline conditions, the performance of the iron (II) oxalate catalyst is much reduced so that the amount of glycerol converted is low and formic acid is not formed. This shows that pH can influence the efficiency of H_2O_2 as an oxidant, as Crotti and Farnetti [17] reported.

The influence of reaction temperature as one of the crucial parameters in the reaction was investigated in this study in the room temperature range up to 90°C at atmospheric pressure (compare numbers 1 and 9 and 5, 10 and 11 in Table 1). At room temperature, the glycerol oxidation reaction at pH five could only produce a conversion of 67.87% with a yield and formic acid selectivity of 23.30% and 34.33%, respectively (Table 1 number 1). When the reaction temperature was increased to 50°C, the amount of glycerol converted increased to 83.18%, accompanied by an increase in the yield and selectivity of the formic acid product produced by 47.77% and 57.43%, respectively (Table 1 number 9). This condition provides the best results for the yield and selectivity of the formic acid product produced. The effect of reaction temperature on the glycerol oxidation process is shown in Figure 3.

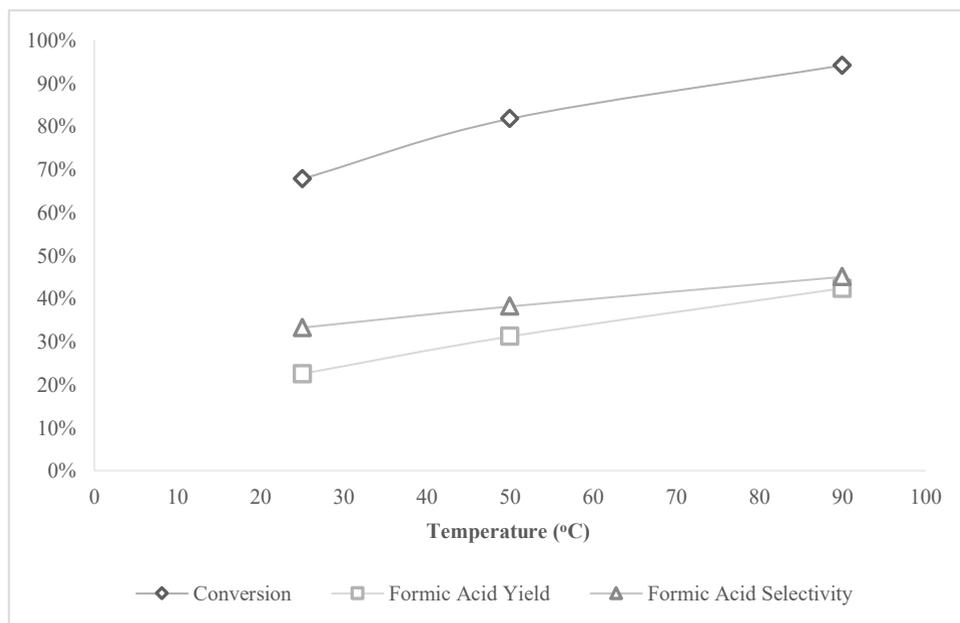


Fig. 3. Effect of reaction temperature on formic acid's conversion, yield, and selectivity.

At pH 3, increasing the temperature from room temperature to 50°C also increases the glycerol conversion and the yield and selectivity of formic acid. Increasing the reaction temperature to 50°C caused formic acid's conversion, yield, and selectivity to increase to 81.69%, 31.15%, and 38.14%, respectively. This result is lower when compared to the result

of glycerol oxidation at pH 5 for the same increase in reaction temperature. A further increase in temperature to 90°C further increased the glycerol conversion along with the yield and selectivity of formic acid to reach 94.10%, 42.35%, and 45.01%, respectively. These results indicate that high temperatures of up to 90°C at atmospheric pressure are required for the glycerol oxidation reaction to produce formic acid using an iron (II) oxalate catalyst.

4 Conclusion

Based on the research results presented, it can be concluded that the iron (II) oxalate effectively catalyses the glycerol oxidation process to produce formic acid with high conversion under appropriate reaction conditions. High glycerol conversion of 83.18% with formic acid yield and selectivity of 47.77% and 57.43%, respectively, can be obtained under mild experimental conditions, namely at a temperature of 50°C (atmospheric pressure) and initial solution pH of 5 with time reaction for 240 minutes.

References

1. W. Wang, M. Niu, Y. Hou, W. Wu, Z. Liu, Q. Liu, S. Ren, K.N. Marsh, *Green Chem.*, **16**, 2614-2618 (2014).
2. J. Xu, Y. Zhao, H. Xu, H. Zhang, B. Yu, L. Hao, Z. Liu, *Appl. Cat. B: Env.*, **154–155**, 267–273 (2014).
3. N. M. Aslam, M. S. Masdar, S. K. Kamarudin, W. R. W. Daud, *APCBEE Procedia*, **3**, 33-39 (2012).
4. I. Schmidt, K. Müller, W. Arlt, *Energy Fuels*, **28**, 6540–6544 (2014).
5. W. Deng, Q. Zhang, Y. Wang, *Cat. Today*, **234**, 31-41 (2014).
6. M. Czaun, A. Goepfert, J. Kothandaraman, R. B. May, R. Haiges, G.K.S. Prakash, G.A. Olah, *ACS Catal.*, **4**, 311–320 (2014).
7. J. Zhang, M. Sun, Y. Han, *RSC Adv.*, **4**, 35463 (2014).
8. M. Rumayor, A. Dominguez-Ramos, A. Irabien, *Appl. Sci.*, **8**, 914 (2018).
9. Y. L. Zhang, M. Zhang, Z. Shen, J. F. Zhou, *J. Chem. Technol. Biotechnol.*, **88**, 829-833 (2012).
10. P. Palanychamy, S. Lim, Y.H. Yap, L.K. Leong, *Catalysts*, **12**, 1487 (2022).
11. H.W.Tan, A.R. Abdul Aziz, M.K. Aroua, *Renewable and Sustainable Energy Reviews*, **27**, 118–127 (2013).
12. A.T. Kiakalaich, N.A.S. Amin, K. Rajaei, S. Tarighi, *Applied Energy*, **230**, 1347–1379 (2018).
13. E. Farnetti, C. Crotti, *Cat. Comm.*, **84**, 1-4 (2016).
14. A. Furstner, *ACS Cent. Sci.*, **2**, 778-789 (2016).
15. X. Jiang, J. Zhang, S. Ma, *J. Am. Chem. Soc.*, **138**, 27 (2016).
16. A. Guðmundsson, K. E. Schlipköter, Jan-E. Bäckval, *Angew. Chem. Int. Ed.*, **59**, 5403–5406 (2020).
17. C. Crotti, E. Farnetti, *Journal of Molecular Catalysts A: Chemical*, **396**, 353-359 (2015).
18. K. Li, Y. Liang, J. Yang, G. Yang, R. Xuc, X. Xie, *Catal. Sci. Technol.*, **8**, 6057 (2018).

19. J.H. Ramirez, C.A. Costa, L.M. Madeira, G. Mata, M.A. Vicente, M.L.R. Cervantes, R.M.M. Aranda, *App. Cat. B: Environmental*, **71**, 44–56 (2007).
20. S.I. Lee, H.R. Kim, J.K. Park, W. Oh, J. Kim, C. Kim, J. Lee, K.-C. Kim, B.-C. Lee, *Processes*, **10**, 2420 (2022).
21. A. Borges, H. José, V. Homem, M. Simões, *Antibiotics (Basel)*, **9**, 2 (2020).
22. R. A. Sheldon, *Chem. Soc. Rev.*, **41**, 1437–1451 (2012).
23. M. Hermanek, R. Zboril, I. Medrik, J. Pechousek, C. Gregor, *J. Am. Chem. Soc.*, **129**, 35 (2007).