

A Brief Review of Functionalized Metal-Organic Frameworks for Olefin Epoxidation: Catalytic Performance and Structural Stability

Laela Mukaromah^{*a}, Bijak Riyandi Ahadito^a, Yessi Permana^b, Aep Patah^b

^aDepartment of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Ogan Ilir, 30662, Indonesia

^bInorganic and Physical Chemistry Research Group, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Bandung, 40132, Indonesia

REVIEW

Received 06 April 2026

Accepted 19 May 2026

Key word:

Metal-Organic Frameworks

Olefin Epoxidation

Catalytic Performance

Structural Stability

*e-mail:

mukaromah@unsri.ac.id

*Telp: +6285223580948

ABSTRACT

The development of catalytic technologies for olefin epoxidation has attracted attention due to the catalyst's convenient separation after reaction. Metal-organic frameworks emerge as alternative materials for olefin epoxidation via heterogeneous catalysis. However, these materials exhibit lower catalytic performance than commonly used homogeneous catalysts. Efforts to functionalize metal-organic frameworks have been conducted to enhance their catalytic performance. Generally, one-pot synthesis and post-synthetic modification are the two main methods for functionalizing metal-organic frameworks with several functional species, such as transition-metal ions and complex compounds. This review summarizes the catalytic performance and structural stability of functionalized metal-organic frameworks for olefin epoxidation from both modification methods. In addition, this review identifies challenges and offers future research insights into olefin epoxidation.

Introduction

Nowadays, organic chemistry reactions catalyzed by heterogeneous catalysts represent a promising breakthrough for overcoming the complex separation of homogeneous catalysts [1]. Previously, several chemical reactions, such as epoxidation [2], acetalization [3], and isomerization [4], have been reported to use homogeneous catalysts, particularly transition-metal-based complexes. Despite the limitations of homogeneous catalysts, they are still widely employed due to their superior catalytic performance [5]. Thus, efforts have been initiated to minimize the dependence on homogeneous catalysts by gradually switching to heterogeneous catalysts that offer high catalytic performance and convenient separation [6].

Metal-organic frameworks (MOFs) are evolving to be suitable materials for heterogeneous catalysts [7]. MOFs are porous inorganic materials composed of metal-ion clusters and organic linkers held together by coordination bonds [8]. These materials possess significant chemical and physical properties,

such as tunable structures and facile modification, which are beneficial for catalytic performance [9,10]. MOFs can be used directly or indirectly as heterogeneous catalysts, namely pristine and functionalized MOFs, respectively. Chemical reactions, such as epoxidation, catalyzed by pristine and functionalized MOFs have been investigated [11–14].

Epoxidation of olefins is a significant reaction for producing epoxides, which are important intermediates in various fine chemical industries [15]. Beforehand, olefin epoxidation is mostly carried out with early transition-metal-based catalysts such as titanium, vanadium, molybdenum, and manganese [16,17]. However, these homogeneous catalysts offer excellent conversion and selectivity; their difficult separation likely limits the balance between economic and environmental considerations [5]. Therefore, immobilizing complex compounds within MOFs has been developed to address the shortcomings of homogeneous catalysts [18–20].

Herein, recent advances in the catalytic performance and structural stability of functionalized MOFs for olefin epoxidation prepared via one-pot synthesis and post-synthetic modification (PSM) are reported. Subsequently, the functionalization of MOFs with transition-metal ions was also elucidated. In addition, the defects within the frameworks of functionalized MOFs and their relationship to active-site formation and catalytic behavior were briefly discussed. Furthermore, the future insight was provided for further research.

Functionalization of Metal-Organic Frameworks

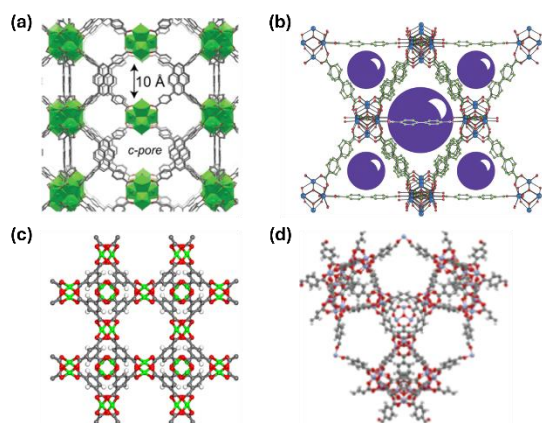


Figure 1. The structures of (a) NU-1000, reproduced with permission [29], copyright 2021 Inorganic Chemistry, (b) UiO-67, reproduced with permission [31], copyright 2013 Chemical Communications, (c) HKUST-1, reproduced with permission [32], copyright 2014 The Journal of Physical Chemistry C, (d) MIL-101(Cr), reproduced with permission [33], copyright 2016 ACS Sustainable Chemistry & Engineering Journal.

Over 100,000 crystal structures of metal-organic frameworks (MOFs) are collected in the Cambridge Structural Database. Several MOFs are named after the university that first reported them, i.e., UiO (University of Oslo), MIL (Material Institute of Lavoisier), DUT (Dresden University of Technology), NU (Northwestern University), and HKUST (Hong Kong University of Science and Technology). These

series exhibit outstanding catalytic performance across many applications, especially in catalysis [21–25]. UiO-series MOFs like UiO-66 and UiO-67 are constructed from zirconium(IV) metal clusters of $Zr_6O_4(OH)_4$, connected by 1,4-benzenedicarboxylate (BDC) and 4,4'-biphenyldicarboxylate (BPDC) organic ligands, respectively [26,27]. DUT-52 and NU-1000 are also zirconium(IV)-based MOFs linked to 2,6-naphthalenedicarboxylate (NDC) and 1,3,6,8-(*p*-benzoate)pyrene (TBAPy) ligands, respectively [28,29]. MIL-101(Cr) is one of chromium(III)-based MOFs with BDC ligand [30]. HKUST-1 is copper(II)-based MOFs linked to 1,3,5-benzenetricarboxylate (BTC) ligand [23]. The structures of MOFs are shown in Figure 1.

The use of MOFs for various chemical reactions aligns with their excellent catalytic performance, including high conversion and selectivity, as well as catalyst reusability [22,34]. These properties are crucial for the long-term and large-scale use of the catalyst, particularly at the industrial level [35]. MOFs have been identified as suitable support materials for homogeneous catalysts in various chemical reactions, particularly for olefin epoxidation [20,34,36]. Aside from complex compounds, MOFs can also be functionalized with metal oxides, ionic liquids, polyoxometalates, and transition-metal ions [15,37–39].

In general, the functionalization of MOFs with transition metal ions or complex compounds has been reported using one-pot synthesis and PSM methods. A one-pot synthesis method fabricates functionalized MOFs by directly dissolving the functional species into a mixture of MOF precursors, then heating the mixture under solvothermal conditions [5]. Meanwhile, the PSM method proceeds in several steps: synthesis of MOFs, followed by the introduction of functional species into their structure. In summary, one-pot synthesis offers shorter reaction times than the PSM method. However, the PSM method allows greater dispersion of functional species within the MOF structure, thereby enhancing catalytic performance [40].

The Catalytic Performance of Functionalized Metal-Organic Frameworks

The epoxidation of olefin changes the double covalent bond of carbon atoms into a three-membered cyclic ether called epoxide through an oxygen-atom transfer reaction [11]. The catalytic performance of functionalized MOFs for olefin epoxidation involves the conversion of olefin and the selectivity of desired epoxides. Yildiz et al. evaluated the functionalization of DUT-5 with Co(II), Mn(II), and Mn(III) complexes using the PSM method, which was used as a catalyst for the aerobic epoxidation of *trans*-stilbene. They employed the 2,2'-bipyridine-5,5'-dicarboxylate (BPyDC) organic ligand to facilitate the immobilization of cobalt and manganese ions. Salicylaldehyde was used to modify the amine-functionalized DUT-5 before the incorporation of metal ions. The *trans*-stilbene epoxidation catalyzed by DUT-5-BPyDC(10)-Co achieved higher conversion (93%) and selectivity (75%) than DUT-5-BPyDC(10)-Mn, using only 0.02% catalyst loading. This result was presumably associated with the metal properties, in which cobalt was more compatible for the epoxidation of *trans*-stilbene than manganese [36].

A functionalization of MOFs by the PSM method for olefin epoxidation was also reported by Zhao et al. UiO-66-(COOH)₂ was incorporated with CuSO₄·5H₂O, Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O metal salts to obtain Cu@UiO-1, Cu@UiO-2, and Cu@UiO-3, respectively. After Cu(II) incorporation, the crystalline structure of the Cu@UiO-(1-3) catalysts remained consistent with that of pristine UiO-66-(COOH)₂, indicating material stability. They studied the epoxidation of cyclooctene using Cu@UiO-(1-3) catalysts. The highest conversion and selectivity of cyclooctene, approximately >99%, was catalyzed by Cu@UiO-1 after 4 h of reaction. This result was associated with the porosity of Cu@UiO-1, with pore volume and surface area values close to those of pristine UiO-66-(COOH)₂. Furthermore, Cu@UiO-1 was shown to catalyze cyclooctene epoxidation, maintaining 99% conversion and selectivity even after 8 runs [41].

The functionalization of zirconium(IV)-based MOFs for olefin epoxidation was also

performed by Noh et al. NU-1000 was functionalized with molybdenum(VI) oxide via solvothermal deposition in MOFs to produce Mo-SIM. This material was utilized as a catalyst for the epoxidation of cyclohexene. After 7 h of reaction, Mo-SIM exhibited 93% conversion and 99% selectivity for cyclohexene. In comparison, the catalytic performance of pristine NU-1000, devoid of molybdenum species, was evaluated for cyclohexene epoxidation. The low conversion of cyclohexene (5%) after 7 h of reaction catalyzed by pristine NU-1000 indicated that molybdenum species significantly contributed to Mo-SIM catalytic performance. The versatility of the Mo-SIM catalyst was examined for the epoxidation of 1-hexene and cis-cyclooctene, with selectivity >99% confirmed. Additionally, the Mo-SIM catalyst maintained its catalytic performance for up to 3 runs [39].

Ghasemiyan et al. reported the functionalization of a zinc-based MOF with a Co(III) complex using a PSM method. ZIF-8 linked by a 2-methylimidazole ligand was functionalized with CoDMG complex to produce CoDMG@ZIF-8 catalyst for olefin epoxidation. The catalytic performance of CoDMG@ZIF-8 was explored in the cyclooctene epoxidation. The catalyst exhibited 96% conversion and 82% selectivity after 24 h of reaction. Compared with pristine ZIF-8 (47% conversion, 63% selectivity), the addition of the CoDMG complex to ZIF-8 significantly improved catalytic performance (conversion: 80%, selectivity: 95%). Further experiments were conducted to evaluate the recyclability of CoDMG@ZIF-8. The catalyst maintained its catalytic performance through 4 runs, with only a slight reduction [6].

Song et al. successfully employed another approach to modify two types of zirconium(IV)-based MOFs for olefin epoxidation. UiO-67 and UiO-BPy (BPy = 2,2'-bipyridine-5,5'-dicarboxylate ligand) were functionalized with polyoxomolybdic cobalt (CoPMA) and polyoxomolybdic acid (PMA) by a one-pot synthesis method. They examined the catalytic performances of CoPMA@UiO and PMA@UiO for cyclooctene epoxidation. CoPMA@UiO-BPy delivered the highest conversion (91%) and selectivity (>99%) after 6 h of reaction. In

addition, CoPMA@UiO-BPy also demonstrated exceptional recyclability and stability compared to CoPMA@UiO-67. The presence of the BPy ligand within the UiO-BPy framework contributed to the catalyst's enhanced stability. Besides that, the uniform distribution of CoPMA inside the cages of UiO-BPy frameworks delivered the high catalytic performance of CoPMA@UiO-BPy for cyclooctene epoxidation [15].

Similar to Song's approach, Hu et al. also used a one-pot synthesis to modify UiO-66 with transition-metal heteropolyacids (TM-HPAs) for olefin epoxidation. UiO-66 was functionalized with Fe, Co, Ni, and Cu monosubstituted phosphomolybdic acids to obtain four different TM-HPA@UiO-66 catalysts. The crystalline structures of TM-HPA@UiO-66 were in accordance with the pristine UiO-66, indicating the UiO-66 framework was stable upon the incorporation of TM-HPA. They investigated the catalytic performance of these catalysts for the epoxidation of styrene. Among them, Co-HPA@UiO-66 delivered the highest conversion and selectivity of styrene by 96% and 82%, respectively, after 2 h of reaction. This result could be attributed to the cage size of the UiO-66 framework, which facilitates the confinement of Co-HPA clusters and thereby enables the efficient conversion of styrene to the corresponding epoxide [42].

Jin et al. reported the functionalization of UiO-66 with Mo(VI) via a one-pot synthesis method. They synthesized several Mo@UiO-66 catalysts using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as the Mo(VI) source. Two different modulators, namely formic acid (For) and acetic acid (Ac), were used to control the framework defects in UiO-66. These catalysts were employed for the epoxidation of cyclohexene. The results showed that Mo@UiO-66-100For exhibited the best catalytic performance among all other catalysts. This performance was likely associated with the

strong Lewis acidity of Mo@UiO-66-100For, along with the suitable porosity of pristine UiO-66, which enabled high Mo(VI) dispersion and led to efficient epoxidation of cyclohexene. Furthermore, this catalyst maintained consistent performance for up to 4 runs [5].

The encapsulation of several transition-metal species, including Mo, Co, and Cu, within pristine MOFs significantly enhanced catalytic performance for olefin epoxidation. The Mo(VI) species acts as a Lewis acid, promoting the epoxidation of the olefin via a heterolytic mechanism [19]. The Co(III) species forms a tert-butyl peroxy radical via homolytic cleavage of O_2 , which then reacts with the olefin to produce an epoxide [6]. Subsequently, the Cu(II) species acts as an active intermediate via a radical chain mechanism to form epoxide [42].

The functionalized MOFs exhibit better catalytic performance than the pristine MOFs for epoxidizing olefins. Both one-pot synthesis and PSM methods have been used to functionalize pristine MOFs with various functional groups. Moreover, these catalysts maintain their catalytic performance in terms of conversion and selectivity over several runs, indicating that functionalization of pristine MOFs is necessary for catalytic applications. In addition, the PSM method provided a better distribution of the functional active site within the structure of pristine MOFs compared to the one-pot synthesis method [6,36,39]. The uniform dispersion of the active sites, confirmed by EDX mapping, increased substrate accessibility, leading to efficient catalytic performance of the functionalized MOFs and further explaining the stable structure of pristine MOFs upon modification by this method [41]. The reported catalytic performance for olefin epoxidation using several pristine and functionalized MOFs is summarized in Table 1.

Table 1. Catalytic Performance of Pristine and Functionalized MOFs for Olefin Epoxidation

Catalyst	Substrate	Conv. (%)	Sel. (%)	Reaction Condition	Oxidant	Ref.
NU-1000	Cyclohexene	5	86	60 °C, 7 h, N ₂ atmosphere	TBHP	[39]
Mo-SIM	Cyclohexene	93	99			
UiO-66-NH ₂	Cyclooctene	11	68	80 °C, 24 h	TBHP	[40]
UiO-66-sal-MoA	Cyclooctene	99	99			
UiO-66-sal-MoD	Cyclooctene	99	99			
UiO-66-(COOH) ₂	Cyclooctene	13	99	40 °C, 4 h	O ₂	[41]
Cu@UiO-1	Cyclooctene	99	99			
Cu@UiO-3	Cyclooctene	96	99			
Zr-MOF-bpy	Cyclooctene	23	87	90 °C, 12 h	TBHP	[43]
Zr-MOF-bpy-CuBr ₂	Cyclooctene	88	95			
CuBTC	Cyclooctene	46	50	60 °C, 2 h	TBHP	[44]
Mo-AMP-CuBTC	Cyclooctene	99	99			
ZIF-8	Cyclooctene	47	43	60 °C, 24 h	TBHP	[6]
CoDMG@ZIF-8	Cyclooctene	96	82			
Cu ₃ BTC ₂ -AMP-PA-Mo	Cyclooctene	95	99	90 °C, 3 h	TBHP	[18]
Cu ₃ BTC ₂ -AMP-PA-V	Cyclooctene	77	99			
CoPMA@UiO-bpy	Cyclooctene	91	99	70 °C, 6 h	H ₂ O ₂	[15]
CoPMA@UiO-67	Cyclooctene	82	99			
UiO-67-MoO ₂ Cl ₂ (bpydc)	Cyclooctene	97	100	75 °C, 24 h	TBHP	[45]
PMO ₁₁ Co@UiO-66	Cyclohexene	55	69	60 °C, 6 h	TBHP	[46]
PMO ₁₁ Co@UiO-66	Cyclooctene	68	99			

The Structural Stability of Functionalized Metal-Organic Frameworks

The structural stability of functionalized MOFs after the catalytic olefin epoxidation reaction is also important to examine. For instance, the structural stability of functionalized MOFs can be affected by the thermal stability of pristine MOFs, the functionalization species, and the catalytic reaction temperature. Several catalytic reactions were carried out at high temperatures, which could lead to the leaching of functionalized species or the collapse of the frameworks. On the other hand, the structural stability of functionalized MOFs as catalysts also correlates with their catalytic performance over several runs.

Berijani et al. evaluated the structural stability of [C-NU-1000-Mo] catalyst for styrene epoxidation. There were no significant changes in the structure of the recycled catalyst after 5 runs compared to the fresh catalyst, as indicated by PXRD analysis. It can be concluded that the recovered [C-NU-1000-Mo] holds an intact crystal structure. [C-NU-1000-Mo] was also proven as a stable functionalized Zr-MOFs following the BET analysis [25]. Moreover, the molybdenum ions showed no leaching up to 5 runs. The structural alteration and leaching possibility of Mo(*n*-STI)/M-MOF catalyst (*M* = Zr, Hf) were studied by Gomes et al. The PXRD analysis showed no loss of crystallinity after the contact test with TBHP in TFT. SEM-EDS analysis confirmed the confinement of Mo(CO)₆ guest within the pore of MOFs. The structure of UiO-66 was also maintained after the catalytic reaction with *cis*-cyclooctene [19].

Zhang et al. reported the structural stability of Zn_{0.1}Co₁-MOF-D2-24 catalyst for α -pinene epoxidation. There was no significant change in the PXRD patterns of recycled catalysts after 6 runs compared with those of the fresh catalysts, indicating the materials retained their intact crystal structure. The sustained catalytic activity of the Zn_{0.1}Co₁-MOF-D2-24 catalyst after 6 runs, with 91.2% conversion and 90.6% selectivity, confirmed that no metal leaching occurred. In addition, SEM analysis showed no considerable change in the lamellar structure and morphology of the recycled catalyst. IR and XPS showed agreement in the

signal peaks of the recycled catalyst with those of the fresh catalyst [38]. Zhu et al. investigated the stability of POV-MOF catalysts for internal and terminal olefins by soaking in different solvents and at different pH values. The PXRD patterns of soaked catalysts showed no backbone collapse, indicating structural stability compared with those of the pristine catalysts [47].

The structural stability of Cu@UiO-66-(COOH)₂ catalyst for aerobic epoxidation of cyclooctene was investigated by Zhao et al. After 8 runs, the Cu@UiO-1 catalyst with 1.87 wt% copper species maintained catalytic activity, with 99% conversion and 99% selectivity in each recycle. The excellent recyclability of Cu@UiO-1 was supported by PXRD analysis, which showed that the internal structure remained consistent. Furthermore, the leaching test of copper species in the Cu@UiO-1 catalyst, verified by ICP-AES analysis, showed a copper level of 0.04 ppm, indicating no significant loss during the reaction [41].

The structural stability of the Mo-SIM catalyst for cyclohexene epoxidation was studied by Noh et al. The Mo-SIM catalyst, derived from the functionalization of NU-1000 with molybdenum(VI) oxide, demonstrated no leaching of molybdenum species into solution upon recycling. This result was aligned with the ICP-OES measurements: before and after the catalytic process, the amount of molybdenum per node remained consistent at 2.8 ± 0.3 . In addition, the Mo-SIM catalyst showed no decrease in yield up to 3 runs. The exceptional stability of the Mo-SIM catalyst was also confirmed by PXRD patterns, which showed that the crystallinity of the functionalized MOFs remained consistent with that of the pristine NU-1000, indicating the robustness of the parent frameworks. Moreover, SEM-EDS analysis revealed the maintained morphology and dispersity of the Mo-SIM catalyst [39].

The structural stability of functionalized MOFs after multiple catalytic reaction cycles was confirmed by PXRD and SEM analysis. No significant difference between the fresh and reused catalysts, as shown by the PXRD patterns and SEM images, indicated the catalyst stability. Moreover, catalyst stability was aligned with recyclability, as evidenced by

consistent catalytic performance (conversion and selectivity). Figures 2a and 2b, respectively, displayed the PXRD patterns of the reused CoDMG@ZIF-8 and CoPMA@UiO-bpy, which were in agreement with their fresh peak position [6,15]. Meanwhile, SEM images with EDS line scans of the fresh and reused Mo-SIM are shown in Figures 2c and 2d [39].

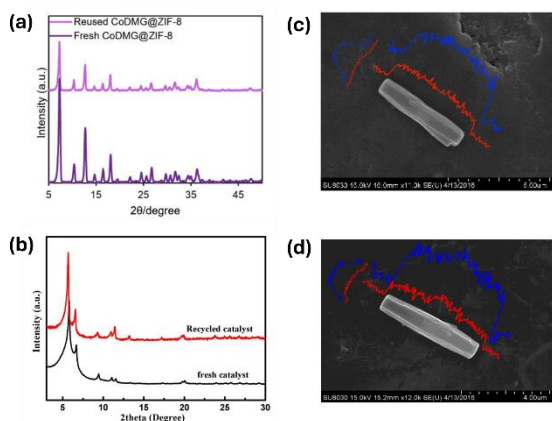


Figure 2. PXRD patterns of (a) CoDMG@ZIF-8, reproduced with permission [6], copyright 2024 Elsevier, (b) CoPMA@UiO-bpy, reproduced with permission [15], copyright 2019 ACS Sustainable Chemistry & Engineering Journal, SEM images of (c) fresh, and (d) reused Mo-SIM (respectively), reproduced with permission [39], copyright 2016 Journal of the American Chemical Society.

The defects within the frameworks of functionalized MOFs also correlated with the catalyst's catalytic behavior. For instance, in the functionalization of UiO-66(Zr/Hf) with $\text{Mo}(\text{CO})_6$ for the epoxidation of *cis*-cyclooctene, functionalized UiO-66(Hf), owing to its higher defectivity, exhibited better recyclability than functionalized UiO-66(Zr). The defect in UiO-66, as the support material, allowed excess loading of the guest species onto the missing linker and the cluster [19]. The structural defect in UiO-66, subsequently functionalized with Mo species, also showed improved catalytic performance in the epoxidation of cyclohexene. Mo@UiO-66-100for displayed the highest catalytic activity at missing-cluster defects,

leading to the efficient epoxidation of cyclohexene [5].

Besides the defect factor, the pore size, metal node, and ligand functionality of the functionalized MOFs also influenced the catalytic outcomes of olefin epoxidation. These factors explained the relationship between the catalyst's structure and activity. Functional species were likely confined within the pores of MOFs rather than on their external surfaces, which served as the catalytic active sites. For example, the pore size of UiO-67, which was larger than that of UiO-66, allowed better accessibility for $\text{Mo}(\text{CO})_6$ incorporation, resulting in the higher catalytic activity [45]. On the other hand, different metal nodes within the isostructural MOFs also contributed to the catalytic performance. For example, UiO-66(Zr) and UiO-66(Hf), in which Hf-based was more oxophilic and acidic than Zr-based, resulting in increased activity as a catalyst with a similar loading of Mo [19]. It was also reported that the ligand functionality affected the immobilization of functional species, such as Mo(VI) complexes, via adduct formation, thereby enhancing catalytic activity [48].

As explained previously, the structural stability of functionalized MOFs also encompasses aspects of metal leaching and robustness of the frameworks. In this case, the functionalization method helped mitigate these issues. The PSM method exhibited high dispersion of functional species on the framework and enabled the formation of a chelating group on the linker, thereby improving catalytic performance [40,43]. The PSM method ensured the robustness of the frameworks during the stepwise functionalization process, thereby preventing metal leaching from the functional groups. On the other hand, the one-pot synthesis method mainly offered shorter reaction times but required higher reaction temperatures to produce pristine MOFs. In short, the PSM method minimized damage to the functional species during functionalization by using a lower reaction temperature than the one-pot synthesis method [49].

Acknowledgement

The authors acknowledge the Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, and Inorganic and Physical Chemistry Research Group, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, for support.

Author Contribution

Laela Mukaromah - conceptualization, methodology design, writing – original draft preparation, writing – review and editing. **Bijak Riyandi Ahadito** - methodology design and writing – review and editing. **Yessi Permana** - conceptualization, writing – review and editing and supervision. **Aep Patah** - conceptualization, writing – review and editing and supervision. All authors agree to the final version of the manuscript.

Conclusion and Outlook

The catalytic performance of MOFs in olefin epoxidation has increased upon functionalization with various active species, such as transition-metal ions and complex compounds, incorporated into the frameworks. In general, one-pot synthesis and post-synthetic modification are the two main methods for functionalizing MOFs. The functionalized MOFs exhibit structural stability comparable to that of the pristine MOFs and excellent recyclability after several runs. However, it should be noted that defects within the frameworks of certain MOFs may influence the dispersion of active species. The uniform distribution of active species and the availability of suitable cages in MOFs significantly enhance their catalytic performance. The catalytic performance of other functionalized MOFs prepared with green chemistry methods needs to be explored. In addition, the use of green oxidants, the low-temperature process, and the catalyst's scale-up challenges must be discussed. Furthermore, the reaction mechanism is also important to examine. The development of heterogeneous catalysts will have a significant impact on large-scale applications in the future.

References

1. Gao, T.; Sun, W.; Wang, H.; Zhang, J.; Yan, Z.; Trentesaux, M.; Marinova, M.; Wang, C.; Ordonsky, V.; Paul, S. Synthesis of a Heterogeneous 2D COF-Based Fenton Catalyst for Epoxidation of Olefins. *Journal of Catalysis* **2025**, 449, 116217, <https://doi.org/10.1016/j.jcat.2025.116217>.
2. Botubol-Ares, J.M.; Hanson, J.R.; Hernández-Galán, R.; Collado, I.G. Mild Epoxidation of Allylic Alcohols Catalyzed by Titanium(III) Complexes: Selectivity and Mechanism. *ACS Omega* **2017**, 2, 3083–3090, <https://doi.org/10.1021/acsomega.7b00386>.
3. Liu, H.; Liu, L.; Guo, W.-D.; Lu, Y.; Zhao, X.-L.; Liu, Y. Phosphine-Ligated Ir(III)-Complex as a Bi-Functional Catalyst for One-Pot Tandem Hydroformylation-Acetalization. *Journal of Catalysis* **2019**, 373, 215–221, <https://doi.org/10.1016/j.jcat.2019.04.004>.
4. Smarun, A. V.; Shahreel, W.; Pramono, S.; Koo, S.Y.; Tan, L.Y.; Ganguly, R.; Vidović, D. Influence of Increasing Steric Demand on Isomerization of Terminal Alkenes Catalyzed by Bifunctional Ruthenium Complexes. *Journal of Organometallic Chemistry* **2017**, 834, 1–9, <https://doi.org/10.1016/j.jorganchem.2017.01.023>.
5. Jin, M.; Liu, G.; Si, C.; Lv, Z.; Cheng, X.; Han, H.; Niu, Q. Molybdenum Active Sites Implanted Defective UiO-66(Zr) for Cyclohexene Epoxidation: Activity and Kinetics Investigation. *Molecular Catalysis* **2022**, 524, 112312, <https://doi.org/10.1016/j.mcat.2022.112312>.
6. Ghasemiyan, M.; Abbasi, A.; Hosseini, M.S. Facile Encapsulation of a Cobalt Complex inside the Micropores of ZIF-8 through the Bottle around the Ship Method: A Novel Heterogeneous Catalyst for Epoxidation of Alkenes. *Journal of Molecular Structure* **2024**, 1311, 138413, <https://doi.org/10.1016/j.molstruc.2024.138413>.
7. Koner, S. Catalytic Epoxidation of Olefin over Metal-Organic Framework Solids: A Mini-Review. *Journal of Organometallic Chemistry* **2025**, 1025, 123449,

- <https://doi.org/10.1016/j.molstruc.2024.138413>.
8. Mukaromah, L.; Haryanto, A.; Permana, Y.; Patah, A. Enhancing the CO₂ Adsorption Performance of UiO-66 by Imidazolium-Based Room-Temperature Ionic Liquids (RTILs) Incorporation. *Indonesian Journal of Chemistry* **2023**, *23*, 1406–1414, <https://doi.org/10.22146/ijc.84669>.
9. Haryanto, A.; Mukaromah, L.; Permana, Y.; Patah, A. Photocatalytic Activity of CuBDC and UiO-66 MOFs for Methyl Orange Degradation. *Journal of Chemical Technology and Metallurgy* **2021**, *53*, 791–795. <https://doi.org/10.59957/jctm>.
10. Agusta, K.D.; Miharja, M.F.; Sakti, A.W.; Arrozi, U.S.F.; Mukaromah, L.; Patah, A.; Hara, T.; Permana, Y. Zr-MOFs–Catalyzed Transfer Hydrogenation of Furfural to Furfuryl Alcohol: Unveiled Performance of DUT-52. *Molecular Catalysis* **2022**, *524*, 112265, <https://doi.org/10.1016/j.mcat.2022.112265>.
11. Moghadaskhou, F.; Hosseini, A.K.; Tadjarodi, A.; Abroudi, M. Amino-Induced Cadmium Metal–Organic Framework Based on Thiazole Ligand as a Heterogeneous Catalyst for the Epoxidation of Alkenes. *Scientific Reports* **2023**, *13*, 15391, <https://doi.org/10.1038/s41598-023-42666-1>.
12. Zhang, H.; Sun, F.; Lu, X.; Guo, H.; Dong, Y.; Zhang, Q.; Chen, J.; Zhou, D.; Xia, Q. Acidic Bimetallic LaCo-MOF Materials Showing Synergistic Catalytic Effect on the Air Epoxidation of Cyclooctene. *Molecular Catalysis* **2023**, *535*, 112903, <https://doi.org/10.1016/j.mcat.2022.112903>.
13. Wang, S.; Liu, Y.; Zhang, Z.; Li, X.; Tian, H.; Yan, T.; Zhang, X.; Liu, S.; Sun, X.; Xu, L.; et al. One-Step Template-Free Fabrication of Ultrathin Mixed-Valence Polyoxovanadate-Incorporated Metal–Organic Framework Nanosheets for Highly Efficient Selective Oxidation Catalysis in Air. *ACS Applied Materials and Interfaces* **2019**, *11*, 12786–12796, <https://doi.org/10.1021/acsami.9b00908>.
14. Stubbs, A.W.; Braglia, L.; Borfecchia, E.; Meyer, R.J.; Román-Leshkov, Y.; Lamberti, C.; Dincă, M. Selective Catalytic Olefin Epoxidation with Mn^{II}-Exchanged MOF-5. *ACS Catalysis* **2018**, *8*, 596–601, <https://doi.org/10.1021/acscatal.7b02946>.
15. Song, X.; Hu, D.; Yang, X.; Zhang, H.; Zhang, W.; Li, J.; Jia, M.; Yu, J. Polyoxomolybdic Cobalt Encapsulated within Zr-Based Metal–Organic Frameworks as Efficient Heterogeneous Catalysts for Olefins Epoxidation. *ACS Sustainable Chemistry & Engineering* **2019**, *7*, 3624–3631, <https://doi.org/10.1021/acssuschemeng.8b06736>.
16. Pandhare, S.L.; Jadhaio, R.R.; Puranik, V.G.; Joshi, P. V.; Capet, F.; Dongare, M.K.; Umbarkar, S.B.; Michon, C.; Agbossou-Niedercorn, F. Molybdenum(VI) Dioxo Complexes for the Epoxidation of Allylic Alcohols and Olefins. *Journal of Organometallic Chemistry* **2014**, *772*, 271–279, <https://doi.org/10.1016/j.jorganchem.2014.09.029>.
17. Mirzaee, M.; Bahramian, B.; Gholizadeh, J.; Feizi, A.; Gholami, R. Acetylacetonate Complexes of Vanadium and Molybdenum Supported on Functionalized Boehmite Nano-Particles for the Catalytic Epoxidation of Alkenes. *Chemical Engineering Journal* **2017**, *308*, 160–168, <https://doi.org/10.1016/j.cej.2016.09.055>.
18. Zamani, S.; Abbasi, A.; Masteri-Farahani, M. Post Synthetic Modification of Porous [Cu₃(BTC)₂] (BTC=benzene-1,3,5-tricarboxylate) Metal Organic Framework with Molybdenum and Vanadium Complexes for the Epoxidation of Olefins and Allyl Alcohols. *Reaction Kinetics, Mechanisms and Catalysis* **2021**, *132*, 235–250, <https://doi.org/10.1007/s11144-020-01912-7>.
19. Gomes, D.P.; Silva, A.F.; Gomes, A.C.; Neves, P.; Valente, A.A.; Gonçalves, I.S.; Pillinger, M. Epoxidation Catalysts Prepared by Encapsulation of Molybdenum Hexacarbonyl in UiO-66(Zr/Hf)-Type Metal–Organic Frameworks. *Microporous and Mesoporous*

- Materials* **2022**, *330*, 111603, <https://doi.org/10.1016/j.micromeso.2021.111603>.
20. Bravo-Sanabria, C.A.; Solano-Delgado, L.C.; Valdivieso-Zarate, L.M.; Ospina-Ospina, R.; Martínez-Ortega, F.; Ramírez-Caballero, G.E. Photo-Epoxidation of α -Pinene Catalyzed by a Mo^{VI} Oxo-Diperoxo Complex Modified Ti-Based Metal-Organic Framework. *Molecular Catalysis* **2023**, *545*, 113240. <https://dx.doi.org/10.2139/ssrn.4314800>
21. Li, W.; Wang, K.; Huang, J.; Liu, X.; Fu, D.; Huang, J.; Li, Q.; Zhan, G. MxOy–ZrO₂ (M = Zn, Co, Cu) Solid Solutions Derived from Schiff Base-Bridged UiO-66 Composites as High-Performance Catalysts for CO₂ Hydrogenation. *ACS Applied Materials and Interfaces* **2019**, *11*, 33263–33272, <https://doi.org/10.1021/acsami.9b11547>.
22. Nikseresht, A.; Ghoochi, F.; Mohammadi, M. Postsynthetic Modification of Amine-Functionalized MIL-101(Cr) Metal-Organic Frameworks with an EDTA-Zn(II) Complex as an Effective Heterogeneous Catalyst for Hantzsch Synthesis of Polyhydroquinolines. *ACS Omega* **2024**, *9*, 28114–28128, <https://doi.org/10.1021/acsomega.4c01117>.
23. Ye, R.-P.; Lin, L.; Chen, C.-C.; Yang, J.-X.; Li, F.; Zhang, X.; Li, D.-J.; Qin, Y.-Y.; Zhou, Z.; Yao, Y.-G. Synthesis of Robust MOF-Derived Cu/SiO₂ Catalyst with Low Copper Loading via Sol–Gel Method for the Dimethyl Oxalate Hydrogenation Reaction. *ACS Catalysis* **2018**, *8*, 3382–3394, <https://doi.org/10.1021/acscatal.8b00501>.
24. Wang, G.; Leus, K.; Hendrickx, K.; Wieme, J.; Depauw, H.; Liu, Y.; Speybroeck, V. Van; Voort, P. Van Der A Series of Sulfonic Acid Functionalized Mixed-Linker DUT-4 Analogues: Synthesis, Gas Sorption Properties and Catalytic Performance. *Dalton Transactions* **2017**, *46*, 14356–14364, <https://doi.org/10.1039/c7dt02752d>.
25. Berijani, K.; Morsali, A.; Hupp, J.T. An Effective Strategy for Creating Asymmetric MOFs for Chirality Induction: A Chiral Zr-Based MOF for Enantioselective Epoxidation. *Catalysis Science and Technology* **2019**, *9*, 3388–3397, <https://doi.org/10.1039/c9cy00565j>.
26. DeStefano, M.R.; Islamoglu, T.; Garibay, S.J.; Hupp, J.T.; Farha, O.K. Room-Temperature Synthesis of UiO-66 and Thermal Modulation of Densities of Defect Sites. *Chemistry of Materials* **2017**, *29*, 1357–1361, <https://doi.org/10.1021/acs.chemmater.6b05115>.
27. Xue, W.L.; Wang, L.; Li, Y.K.; Chen, H.; Fu, K.X.; Zhang, F.; He, T.; Deng, Y.H.; Li, J.R.; Wan, C.Q. Reticular Chemistry for Ionic Liquid-Functionalized Metal-Organic Frameworks with High Selectivity for CO₂. *ACS Sustainable Chemistry and Engineering* **2020**, *8*, 18558–18567, <https://doi.org/10.1021/acssuschemeng.0c06551>.
28. Kesuma, R.F.; Patah, A.; Permana, Y. Microwave-Assisted Synthesis of DUT-52 and Investigation of Its Photoluminescent Properties. *Bulletin of Chemical Reaction Engineering & Catalysis* **2019**, *14*, 124–129, <https://doi.org/10.9767/bcrec.14.1.2369.124-129>.
29. Otake, K.I.; Ahn, S.; Knapp, J.; Hupp, J.T.; Notestein, J.M.; Farha, O.K. Vapor-Phase Cyclohexene Epoxidation by Single-Ion Fe(III) Sites in Metal-Organic Frameworks. *Inorganic Chemistry* **2021**, *60*, 2457–2463, <https://doi.org/10.1021/acs.inorgchem.0c03364>.
30. Leng, K.; Sun, Y.; Li, X.; Sun, S.; Xu, W. Rapid Synthesis of Metal-Organic Frameworks MIL-101(Cr) Without the Addition of Solvent and Hydrofluoric Acid. *Crystal Growth and Design* **2016**, *16*, 1168–1171, <https://doi.org/10.1021/acs.cgd.5b01696>.
31. Katz, M.J.; Brown, Z.J.; Colón, Y.J.; Siu, P.W.; Scheidt, K.A.; Snurr, R.Q.; Hupp, J.T.; Farha, O.K. A Facile Synthesis of UiO-66, UiO-67 and Their Derivatives. *Chemical Communications* **2013**, *49*, 9449–9451, <https://doi.org/10.1039/c3cc46105j>.
32. Perry, J.J.; Teich-Mcgoldrick, S.L.; Meek, S.T.; Greathouse, J.A.; Haranczyk, M.; Allendorf, M.D. Noble Gas Adsorption in Metal-Organic Frameworks Containing Open Metal Sites. *Journal of Physical Chemistry C* **2014**, *118*, 11685–11698,

- <https://doi.org/10.1021/jp501495f>.
33. Darunte, L.A.; Oetomo, A.D.; Walton, K.S.; Sholl, D.S.; Jones, C.W. Direct Air Capture of CO₂ Using Amine Functionalized MIL-101(Cr). *ACS Sustainable Chemistry and Engineering* **2016**, *4*, 5761–5768, <https://doi.org/10.1021/acssuschemeng.6b01692>.
34. Chen, Y.; Zhang, X.; Wang, X.; Drout, R.J.; Mian, M.R.; Cao, R.; Ma, K.; Xia, Q.; Li, Z.; Farha, O.K. Insights into the Structure-Activity Relationship in Aerobic Alcohol Oxidation over a Metal-Organic-Framework-Supported Molybdenum(VI) Catalyst. *Journal of the American Chemical Society* **2021**, *143*, 4302–4310, <https://doi.org/10.1021/jacs.0c12963>.
35. Afzali, N.; Kardanpour, R.; Zadehahmadi, F.; Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Mechler, A.; Mohammadpoor-Baltork, I.; Bahadori, M. Molybdenum(VI)-Functionalized UiO-66 Provides an Efficient Heterogeneous Nanocatalyst in Oxidation Reactions. *Applied Organometallic Chemistry* **2019**, *33*, 5225, <https://doi.org/10.1002/aoc.5225>.
36. Yildiz, C.; Kutonova, K.; Oßwald, S.; Titzel-Alonso, A.; Bitzer, J.; Bräse, S.; Kleist, W. Post-Synthetic Modification of DUT-5-Based Metal Organic Frameworks for the Generation of Single-Site Catalysts and Their Application in Selective Epoxidation Reactions. *ChemCatChem* **2020**, *12*, 1134–1142, <https://doi.org/10.1002/cctc.201901434>.
37. Jin, M.; Niu, Q.; Liu, G.; Lv, Z.; Si, C. Encapsulation of Ionic Liquids into POMs-Based Metal–Organic Frameworks: Screening of POMs-ILs@MOF Catalysts for Efficient Cycloolefins Epoxidation. *Journal of Materials Science* **2020**, *55*, 8199–8210, <https://doi.org/10.1007/s10853-020-04611-9>.
38. Zhang, H.; Lu, X.; Yang, L.; Hu, Y.; Yuan, M.; Wang, C.; Liu, Q.; Yue, F.; Zhou, D.; Xia, Q. Efficient Air Epoxidation of Cycloalkenes over Bimetal-Organic Framework ZnCo-MOF Materials. *Molecular Catalysis* **2021**, *499*, 111300, <https://doi.org/10.1016/j.mcat.2020.111300>.
39. Noh, H.; Cui, Y.; Peters, A.W.; Pahls, D.R.; Ortuño, M.A.; Vermeulen, N.A.; Cramer, C.J.; Gagliardi, L.; Hupp, J.T.; Farha, O.K. An Exceptionally Stable Metal–Organic Framework Supported Molybdenum(VI) Oxide Catalyst for Cyclohexene Epoxidation. *Journal of the American Chemical Society* **2016**, *138*, 14720–14726, <https://doi.org/10.1021/jacs.6b08898>.
40. Tang, J.; Dong, W.; Wang, G.; Yao, Y.; Cai, L.; Liu, Y.; Zhao, X.; Xu, J.; Tan, L. Efficient Molybdenum(VI) Modified Zr-MOF Catalysts for Epoxidation of Olefins. *RSC Advances* **2014**, *4*, 42977–42982, <https://doi.org/10.1039/c4ra07133f>.
41. Zhao, J.; Wang, W.; Tang, H.; Ramella, D.; Luan, Y. Modification of Cu²⁺ into Zr-Based Metal–Organic Framework (MOF) with Carboxylic Units as an Efficient Heterogeneous Catalyst for Aerobic Epoxidation of Olefins. *Molecular Catalysis* **2018**, *456*, 57–64, <https://doi.org/10.1016/j.mcat.2018.06.023>.
42. Hu, D.; Song, X.; Zhang, H.; Chang, X.; Zhao, C.; Jia, M. Aerobic Epoxidation of Styrene over Zr-Based Metal-Organic Framework Encapsulated Transition Metal Substituted Phosphomolybdic Acid. *Molecular Catalysis* **2021**, *506*, 111552, <https://doi.org/10.1016/j.mcat.2021.111552>.
43. Toyao, T.; Miyahara, K.; Fujiwaki, M.; Kim, T.H.; Dohshi, S.; Horiuchi, Y.; Matsuoka, M. Immobilization of Cu Complex into Zr-Based MOF with Bipyridine Units for Heterogeneous Selective Oxidation. *Journal of Physical Chemistry C* **2015**, *119*, 8131–8137, <https://doi.org/10.1021/jp512749y>.
44. Abednatanzi, S.; Abbasi, A.; Masteri-Farahani, M. Post-Synthetic Modification of Nanoporous Cu₃(BTC)₂ Metal-Organic Framework via Immobilization of a Molybdenum Complex for Selective Epoxidation. *Journal of Molecular Catalysis A: Chemical* **2015**, *399*, 10–17, <https://doi.org/10.1016/j.molcata.2015.01.014>.
45. Neves, P.; Gomes, A.C.; Amarante, T.R.; Paz, F.A.A.; Pillinger, M.; Gonçalves, I.S.; Valente, A.A. Incorporation of a Dioxomolybdenum(VI) Complex in a Zr^{IV}-Based Metal-Organic Framework and Its Application in Catalytic Olefin

- Epoxidation. *Microporous and Mesoporous Materials* **2015**, 202, 106–114, <https://doi.org/10.1016/j.micromeso.2014.09.046>.
46. Hu, D.; Song, X.; Wu, S.; Yang, X.; Zhang, H.; Chang, X.; Jia, M. Solvothermal Synthesis of Co-Substituted Phosphomolybdate Acid Encapsulated in the UiO-66 Framework for Catalytic Application in Olefin Epoxidation. *Chinese Journal of Catalysis* 2021, 42, 356–366. [https://doi.org/10.1016/S1872-2067\(20\)63665-8](https://doi.org/10.1016/S1872-2067(20)63665-8)
 47. Zhu, M.; Bai, X.; Wang, S.; Yang, Y.; Zhang, A.; Yang, J.; Lu, Y.; Li, B.; Liu, S. Polyoxovanadate-Based MOFs: Multi-Site Efficient Catalytic Epoxidation of Olefins. *Journal of Alloys and Compounds* **2025**, 1022, 179861, <https://doi.org/10.1016/j.jallcom.2025.179861>.
 48. Nunes, M.S.; Gomes, A.C.; Neves, P.; Mendes, R.F.; Almeida Paz, F.A.; Lopes, A.D.; Pillinger, M.; Gonçalves, I.S.; Valente, A.A. Molybdenum(VI) Complexes with Ligands Derived from 5-(2-Pyridyl)-2H-Tetrazole as Catalysts for the Epoxidation of Olefins. *Catalysis Today* **2023**, 423, 114273, <https://doi.org/10.1016/j.cattod.2023.114273>.
 49. Kutzscher, C.; Nickerl, G.; Senkovska, I.; Bon, V.; Kaskel, S. Proline Functionalized UiO-67 and UiO-68 Type Metal-Organic Frameworks Showing Reversed Diastereoselectivity in Aldol Addition Reactions. *Chemistry of Materials* **2016**, 28, 2573–2580, <https://doi.org/10.1021/acs.chemmater.5b04575>.



2026 by the authors. Licensee Fullerene Journal of Chem. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) (<http://creativecommons.org/licenses/by/4.0/>).