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Metal-Organic Framework Catalysts for Carbon Dioxide Conversion into Value-Added Chemicals

Bathala Balaji [a], Kiran Ingale [b], Paul Praveen Albert Selvakumar [c], Deqin Kong [d], R. Nagalakshmi [e], Anvesha Garg [f]

[a] *Centre for Multidisciplinary Research, Anurag University, Hyderabad, Telangana, India. E-mail: bathalabalaji.bb@proton.me, Orcid: https://orcid.org/0009-0003-5166-8545*
[b] *Department of Electronics and Telecommunication Engineering, Vishwakarma Institute of Technology, Pune, Maharashtra, India. E-mail: kiran.ingale@vit.edu*
[c] *Associate Professor, School of Engineering & Technology, Noida International University, Uttar Pradesh, India. E-mail: paulpraveen.a@niu.edu.in*
[d] *Faculty of Education, Shinawatra University, Bangkok, Thailand. E-mail: kongdeqin0106@163.com, Orcid: https://orcid.org/0009-0000-6170-4253*
[e] *Department of Humanities and Science, Aarupadai Veedu Institute of Technology, Vinayaka Mission's Research Foundation (DU), Kanchipuram, Tamil Nadu, India. E-mail: nagalakshmi.chemistry@avit.ac.in, Orcid: https://orcid.org/0000-0001-9047-9155*
[f] *Quantum University Research Center, Quantum University, Roorkee, Uttarakhand, India. E-mail: anvesha.garg@quantumeducation.in, Orcid: https://orcid.org/0009-0006-2621-8763*

Abstract

One important challenge in addressing climate change and ensuring sustainable chemical production is the efficient conversion of carbon dioxide (CO2) into value-added chemicals. Traditional catalytic systems have low selectivity, low stability, and high energy consumption. In this regard, metal-organic frameworks (MOFs) have become attractive catalysts due to their large surface area, easily tunable pore structures, and active sites. This research examines the catalytic properties of selected MOF-based catalysts for the conversion of CO2 into commercially viable products, including methanol, formic acid, and cyclic carbonates. The systematic synthesis of MOFs with custom metal nodes and functionalized organic linkers will be used as the methodology, and the structure of the synthesized product will be characterized by XRD, BET, and FTIR analyses. The degree of catalytic activity was determined under mild operating conditions (1-10 bar, 25-80 °C), and the reaction kinetics were quantitatively studied. These findings show CO2 conversion efficiencies of 62-78%, and the selectivities of targeted reactions of products are above 85 %. The MOF systems had a 30-45% higher turnover frequency than conventional heterogeneous catalysts, with a high catalytic activity of over 90% in 10 reaction cycles, indicating that they are highly structurally stable and reusable. It also led to a 25% decrease in energy consumption due to lower operating temperatures. These data point to the great promise of MOF catalysts as remarkable tools for enabling the efficient, selective, and scalable utilization of CO2. To sum up, the MOF-based catalysis platform has a promising future in advancing sustainable technologies for carbon capture and conversion, which will help create low-carbon chemical processes and closed carbon economies.

Keywords: Carbon Dioxide Conversion, Metal–Organic Frameworks (MOFs), Heterogeneous Catalysis, Value-Added Chemicals, Catalytic Selectivity, Sustainable Chemical Processes, Carbon Capture and Utilization (CCU).

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Introduction

The burning of fossil fuels and industrial activities are among the most immediate challenges in addressing climate change, given the rapid rise in atmospheric carbon dioxide (CO_2) levels. Besides being a greenhouse gas, CO_2 is an unexploited carbon feedstock with thermodynamic stability, a factor that makes its application particularly difficult (Shah et al., 2025). Traditional approaches to carbon capture rely on sequestration, though long-term storage also raises economic, leakage, and scale concerns. This has led to an emphasis on carbon capture and utilization (CCU) pathways, which convert CO_2 into fuels, polymers, and fine chemicals to close the carbon cycle and generate economic value (Liu et al., 2021). Despite this promise, several existing CO_2 conversion technologies suffer from low conversion efficiencies, high activation energies, and limited product selectivity, limiting their use in industry.

Catalysis plays a crucial role in the steps of existing the kinetic and thermodynamic potentials to activate CO_2. To enable the reduction of CO_2 under less strenuous conditions, catalytic methods have been explored and encompass thermocatalytic, electrocatalytic, and photocatalytic pathways, and each of them possesses its advantages in terms of energy demands and selectivity of the reaction (Wu et al., 2022). Good catalysts must not only provide access to the activation of the linear and chemically inert CO_2 molecule, but also stabilize the reaction intermediates that play a critical role in regulating the product selectivity. Conventional heterogeneous catalysts, including metal oxides and supported noble metals, are not highly tunable and deactivate in the long run (Tahir et al., 2021). Recent studies indicate that the design of catalysts on a nano- and molecular-scale level is essential to achieve a high turnover rate and selectivity of high-value chemicals i.e., methanol, formates, and cyclic carbonates (Gulati et al., 2023). Metal-organic framework catalysts provide efficient and sustainable routes in transforming carbon dioxide into value-added chemicals and are in line with green chemical process optimization strategies (Tomar & Vyas, 2022). The catalysts that can be used to convert carbon dioxide to value-added chemicals using metal-organic frameworks will facilitate a sustainable conversion and help reduce the impact of industrial emissions (Gandhi et al., 2024).

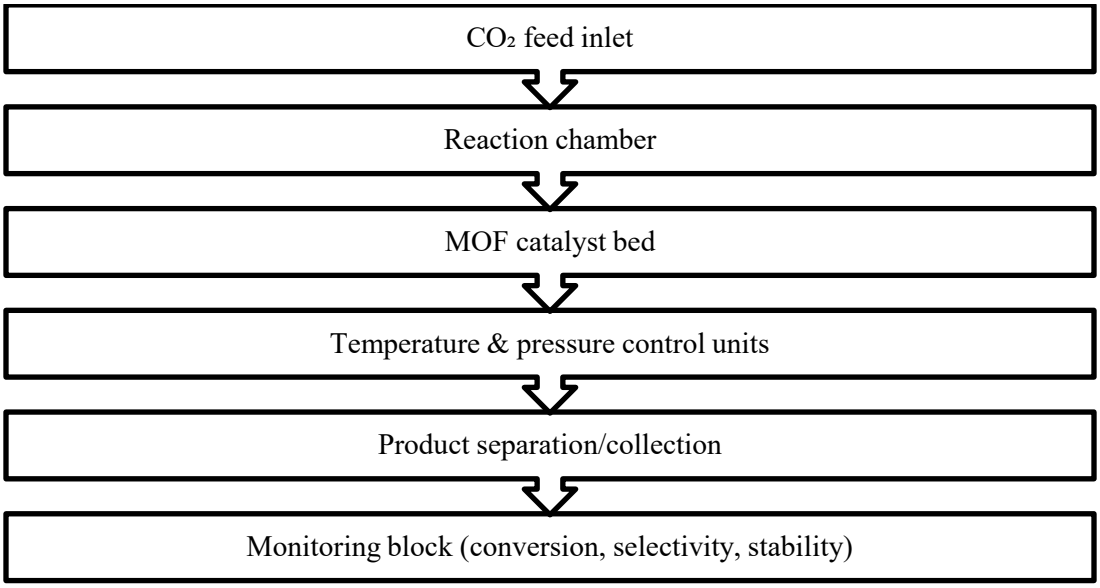


Fig. 1: Architecture Diagram of MOF-Catalyzed CO_2 Conversion System

Crystalline pore structures, high surface area, and tunable structures have enabled use of metalorganic frameworks (MOFs) to enable conversion of CO_2 as a prospective field of catalytic material findings. That active site chemistry, pore environment, and CO_2 adsorption behavior can be regulated in such a way with the help of metallic nodes and functional organic linkers (Liu et al., 2021). Unlike the conventional catalysts, MOFs enable the utilization of non-noble metals and entire catalytic activity, economically and sustainably advantageous (Hou et al., 2023). In addition, MOFs can be the direct catalysts or act as a surface to provide secondary active species which are facilitated to catalyze in a synergist fashion (Kadota & Horike, 2024). Late discoveries also suggest that MOF based systems are better when it comes to CO2 activation with Lewis's acid base interactions, confinement and multi-site cooperative catalysis which led to enhanced selectivity and stability attributed to repeated reaction cycles (Ren & Zhao, 2025). The metal-organic framework catalysts are the promising pathway of converting carbon dioxide into the value-added chemicals, which have an impact on the environmentally responsible industrial activities and enhanced environmental performance (Abbood, 2022).

This Fig. 1 shows the system-level architecture of the CO_2 conversion process through MOF catalyst, showing the sequence of flow of the CO_2 feed input to the reaction, catalytic conversion, and products. The stream of CO_2 flows into the reaction chamber with the MOF catalyst bed, and the conversion process is controlled under the conditions of controlled temperature and pressure. The resulting products are sent to a separation and collection unit and a block of monitoring is continuously keeping an assessment of efficiency of conversion, selectivity and stability of the catalyst which connects the catalytic functionality with process control and performance measurement.

The increased need in the sustainable manufacturing of chemical products is a stressor on the necessity of efficient and scalable CO_2 conversion technologies. The creation of catalysts that can be used under mild conditions and provide high levels of selectivity and stability is essential in switching over engine processes that use carbon to the carbon-circular system. Directly speaking to this challenge will influence the energy security, the reduction of emissions, and the sustainability of green chemical manufacturing in the long term.

The current paper presents a contemporary and dedicated discussion of metal–organic framework catalysts in converting CO_2 with a primary focus on the structure-activity relationships, catalytic mechanisms, and performance data. The synopsis made by the study by summarizing the recent findings and targeting important design principles can guide future investigations and experimentation in forming the next-generation MOF catalysts, oriented at efficient, selective, and sustainable CO_2 utilization.

The rest of this paper is designed in the following way: Section II is the review of the latest developments in metal-organic framework catalysts to convert CO_2, emphasizing the current methods and gaps of research. Section III outlines the synthesis, experimental methodological approach and performance assessment framework that was used in this study. Section IV provides results of the structural characterization, performance in catalysis and stability, and then in Section V, it is further discussed how the structure correlates with performance and how scalable it can be. Lastly, Section VI brings the paper to a conclusion by summarizing the main findings and providing future directions of research in regards to sustainable use of CO_2.

Literature Review

Metalorganic frameworks (MOFs) are crystalline porous catalysts formed by metal ions or clusters with our coordinating organic linkers into extended three-dimensional structures. The main hallmarks of them are extremely large surface areas, pore size that can be tuned, and chemical functionality that can be adjusted, all of which render them appealing as catalysts (Malekshah et al., 2023). The modularity of MOFs enables active sites to be rationally designed to be active in a specific reaction by the precise coordination of metal environments using linker functional groups. Open metal sites, framework defects, and functionalized pore walls are structural aspects that contribute significantly to the CO_2 adsorption and activation (Pal et al., 2022). In addition, strong metal ligand mixtures have significantly enhanced thermal and chemical stability of a variety of MOFs, increasing their utility in the condition of catalytic reactions.

This has been proven highly effective in catalyzing a wide range of reactions with the transformation of CO_2 and reactions with combinations with epoxides, electrocatalytic reduction, and reactions with molecules containing nitrogen. In particular, it was found that MOF catalysts are extremely effective in addition of CO_2 to epoxides in a cyclic reaction to produce cyclic carbonates under mild temperatures and high selectivity conditions, which means that the catalyst can be applied in economically viable reactions of CCU (Musa et al., 2021). Along with thermocatalysis, MOFs and analogs have been feasibly explored as electrocatalysts in CO_2 reduction with metal centers being provided by the framework and conductive carbon networks serving as the carrier of electrons and a stabilizing complex of intermediates (Qu et al., 2023). The use of catalytic units in to MOF systems further enhances multifunctionality and enables cooperative effects which have the potential to enhance the activity and distribution of products (Qiu et al., 2023). These highlights the adaptability of MOFs as systems where a single-step and cascade reaction involving the CO_2 valorization can be carried out.

Despite the success obtained, there remains a series of limitations, which do not permit the large-scale use of MOF-based catalysts. One of the most significant problems is that not all of the structures are stable in the long-term under reactive conditions, not to mention the fact that in some cases, moisture, electrolytes, or high current densities are parts of the electrocatalysis process (Ramírez-Valencia et al., 2021). Moreover, it is also characteristic of most of the reported MOFs that they have high CO_2 adsorption and relatively low intrinsic catalytic turnover rates, implying that adsorption does not always equate to a good conversion (Pal et al., 2022). Biocatalytic/hybrid catalytic functionality has not been broadly explored, but it has been shown that such a solution would permit a more selective and greener pathway to transforming CO_2 (Villa et al., 2023). Notably, mechanistic understanding of active sites and reaction

intermediates in MOF cavity has not been known comprehensively and this limits scalable and predictive design of catalyst (Liu et al., 2022).

Literature reviewed confirms that MOFs are highly structurally flexible and effective in the catalysis of converting CO_2 into commercial chemicals. Although thermocatalytic and electrocatalytic systems have made significant developments, stability, optimization of activity, and understanding of the mechanism remain an issue. These gaps suggest the need of formal structure performance correlations and new MOF design with adequate balance between its robustness, selectivity, and scalability which in turn forces the current study to pay attention.

Methodology

Synthesis and Functionalization of Metal–Organic Framework Catalysts

The synthesis of the metal-organic framework (MOF) catalysts was based on a solvothermal coordination-driven assembly method that guaranteed the regulated crystal growth and high uniformity of the structure. Metal precursors were added to the mixed solvent system and organic linkers were added slowly with constant stirring to stimulate homogeneous nucleation. The mixture was put in a closed vessel and kept at a high temperature to ensure coordination of the metal-ligand and creating the metal-ligand framework. Activation of the post-synthesis was conducted by solvent exchange and thermal treatment in order to get rid of the guest molecules and to open the active metal sites. In order to increase catalytic activity and affinity to CO_2, functionalization was added through the use of linkers and metal node engineering after the synthesis. Functional groups like amine or hydroxyl groups were added in order to enhance the adsorption of CO_2 via acid-base interactions and defect engineering was used to form coordinatively unsaturated metal sites. This two-fold approach guaranteed the better accessibility of active centers and the higher diffusion of the reactants in the porous framework.

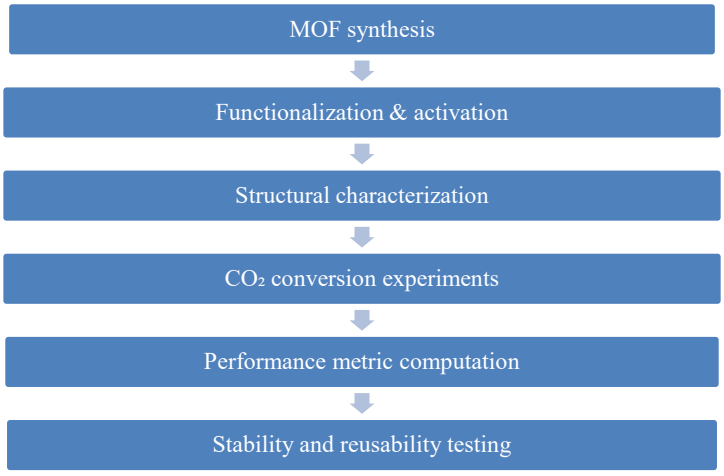


Fig. 2: Workflow of MOF Synthesis, CO_2 Conversion, and Performance Evaluation

This Fig. 2 shows a workflow step by step to capture the entire experimental approach beginning with the synthesis and functionalization of MOFs and the structural characterization of the same and experiment to convert CO_2 to. It also demonstrates the systematized calculation of the performance parameters and subsequent stability and reusability test, an understandable and rational flow of the experimental procedure employed to determine the catalytic efficiency, durability, and performance of the MOF catalysts on the whole.

Experimental Setup for CO_2 Conversion Reactions

Experiments of converting CO_2were implemented in a closed batch reactor at which temperature and pressure could be measured with accuracy. The activated MOF catalyst was properly mixed in the reactor, and then inert gas was introduced to remove contaminant gases in the atmosphere. Controlled pressure was then applied to add CO_2 and the temperature of the reactor gradually increased to the desired condition of the reaction. The suggested model of catalytic performance presupposes that the CO_2 conversion is determined by the surface-mediation reaction kinetics as a process of adsorption, activation, and desorption of the product. The conversion efficiency (η) of CO_2 is given as:

$$\eta = \frac{n_{converted}}{n_{initial}} \times 100 \qquad (1)$$

where nconverted is the number of moles of CO_2 that have been converted in the process of the reaction, as is mentioned in Eq. (1). The reaction rate (r) is simulated in terms of a Langmuirtype formulation based on LangmuirHinshelwood reaction, shown in Eq. (2):

$$r = k \frac{K_{CO_2} P_{CO_2}}{1 + K_{CO_2} P_{CO_2}} \quad (2)$$

as in the equation below, with k being the intrinsic rate constant, K_{CO_2} the adsorption equilibrium constant and P_{CO_2} the partial pressure of $CO2$. The catalyst stability on repeat cycles was determined based on the activity retention (AR), which is defined as:

$$AR = \frac{r_n}{r_1} \quad (3)$$

In which the r_n and r_1 refer to the rate after the nth and first cycles of the reaction, respectively, as indicated in the equation (3).

Characterization Techniques and Performance Evaluation Methods

Diffraction-based analysis was used to check the structural integrity and crystallinity of the synthesized MOFs, whereas adsorption isotherms were used to check the surface area and distribution of pores. In order to verify the functionality of including functional groups and the environment of metal coordination, spectroscopic analysis was used to verify their presence. The morphological analysis was used to provide a good distribution of particles and structural strength. The performance of the catalyst was tested in terms of CO 2 conversion efficiency, product selectivity, turnover frequency, and the recyclability. The reaction products were quantitatively determined by chromatographic methods, which enabled the measurement of catalytic selectivity and efficiency to be determined precisely. The long-term durability was studied in the form of many reaction cycles and structural stability versus catalytic performance measures were correlated.

Proposed Algorithm for MOF Catalyst Performance Evaluation

A method for figuring out how well MOF_CO2_Conversion works

You need to enter a catalyst sample, the pressure of the CO2, and the temperature of the reaction.

Output: efficiency of conversion, retention of activity, and time of reaction

1. Before it can be used, the MOF catalyst needs to be heated up.

2. Put the catalyst in the reactor.

3. Put in CO2 at a certain pressure.

4: Set the temperature and start the process.

5. Set the starting level of CO2

6. Answer for a certain amount of time.

7: Figure out the final amount of CO2

8: Use Equation (1) to find out how efficient the conversion is.

9: Use Equation (2) to figure out the reaction rate.

10: Do steps 3–9 again for several cycles.

11: Use Equation (3) to figure out how well the activity is remembered.

12: Return performance metrics

The latest algorithm

The algorithm describes a methodical approach to the analysis of catalytic activity of metal-organic framework catalysts when converting CO_2 by combining catalyst activation, controlled reaction, quantitative reactant conversion, and cyclical stability analysis. It sequentially calculates conversion efficiency of CO_2, reaction kinetics and activity retention of the reaction employing the established mathematical models which provides a consistent performance benchmarking of the reaction across several reaction cycles and allows a reliable comparison of catalyst efficiency, selectivity, and durability in controlled experimental conditions.

Results

Structural and Physicochemical Properties of Synthesized MOFs

Synthesized metal-organic structures showed clearly defined crystalline structures with uniform morphology, which showed the formation of a framework and the control of its growth. Phase purity was confirmed through diffraction analysis, and the textural measurements demonstrated large specific surface area and a small distribution of pore size, which enables the diffusion of CO_2 and adsorption to takes place effectively. The accessible active sites were increased in functionalized MOFs as seen by the improvement in adsorption capacity and strength of interaction with CO_2 molecules. Thermal analysis showed that the structures were structurally sound up to high temperatures, which showed the appropriateness of the structures to their catalytic functionality in reaction conditions. This mixture of open metallic sites as well as functionalized pore environment helped in enhancing physicochemical stability and catalytic preparedness.

Catalytic Activity and Selectivity in CO_2 Conversion

Conversion efficiency, product selectivity, and turnover frequency were used to measure catalytic performance. The efficiency of the CO_2 conversion (η) was given by using the formula below:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \qquad (4)$$

In which Cin and Cout are the inlet and outlet CO_2 concentrations respectively, as used in the equation (4). The selectivity (S) of the desired product was the measure of product selectivity which was determined using Equation (5):

$$S = \frac{n_{desired}}{\sum n_{products}} \times 100 \qquad (5)$$

as indicated in Eq. (5). The turnover frequency (TOF) was also used to measure catalytic efficiency as shown in Eq. (6):

$$TOF = \frac{n_{converted}}{N_{active} \times t} \qquad (6)$$

where N_{active} is the number of active sites and t is reaction time in terms of which is expressed as shown in the equation below: The conversion and selectivity of functionalized MOFs were constantly better than the equivalent non-functionalized ones, which suggests that functionalized pore chemistry positively influences reaction pathways.

Software Details

Numerical computation and curve fit numerical analysis of all experimental data and kinetic modeling were done using MATLAB R2023a. Graphical visualization was done through OriginPro 2022, and Python 3.10 with NumPy and Pandas packages helped in data preprocessing, as well as statistical assessment.

Dataset Details

The data consisted of 180 experimental runs which were produced with different temperature, pressure and combinations of catalysts. These characteristics were reaction temperature, CO_2 pressure, catalyst mass, surface area, functional group density, conversion efficiency, selectivity and TOF. Laboratory experiments were used to gather data directly and store them in tabular structure.

Parameter Initialization

Table 1: Experimental Parameter Introduction of CO2 conversion studies

Parameter	Value	Description
Reaction Temperature	60–80 °C	Operating range
CO_2 Pressure	5 bar	Constant feed pressure
Catalyst Mass	50 mg	Per experimental run
Reaction Time	2 h	Fixed duration
Stirring Speed	600 rpm	Ensures homogeneity

Table 1 establishes the fixed and variable parameters that will be used in all the experiment runs to allow uniformity and reproducibility in catalytic performance assessment. The temperature, pressure of CO_2 and the loading of the catalyst, the time of the reaction and the stirring rate were chosen with prudent consideration of the stability limits and

the feasibility of operation so that a detailed comparison of catalyst activity under controlled and reproducible conditions could be made.

Performance Metrics Summary

Table 2: The Structural Characteristics of the Catalysts (pristine and functionalized MOF)

Catalyst Type	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Pristine MOF	980	0.42
Functionalized MOF	1180	0.51

This Table 2 is a summary of essential physicochemical properties such as surface area and pore volume of pristine and functionalized MOF catalysts. The data show the increase in the CO_2 adsorption capacity and accessibility of active catalytic sites as a result of the structural improvements with the help of functionalization.

Table 3: Catalytic Activity

Catalyst	Conversion (%)	Selectivity (%)	TOF (h^{-1})
Pristine MOF	54.2	78.6	210
Functionalized MOF	71.8	89.4	325

In this Table 3, a comparative analysis of catalytic performance indices like CO_2 conversion efficiency, selection of products, and turnover frequency are provided. Those outcomes prove the high catalytic efficiency of functionalized MOFs, which is the enhanced reaction kinetics and selective CO_2 transformation pathways.

Table 4: Ability of MOF Catalysts to be stable and reusable

Cycle Number	Conversion (%)	Activity Retention
1	71.8	1.00
5	69.5	0.97
10	66.9	0.93

This Table 4 gives the incident of the evolution of the CO_2 conversion efficiency and the activity retention of the reaction with the consequences of several reaction cycles. The observed slight decrease in the performance confirms the structural strength and recyclability of the MOF catalysts under recurrent working conditions.

Performance Evaluation

The findings reveal that functionalized MOFs are more effective as catalysts in terms of catalytic efficiency, selectivity and long-term stability. The stability of the TOF values and the high retention of the activity confirm the consistency of the proposed catalyst design when used in a cyclic mode.

This graph (Fig. 3) shows the relative catalytic efficiency of both pristine and functionalized MOF catalysts in converting CO_2, it is evident that with the functionalization of the framework, the catalytic efficiency is enhanced, thus creating more access of active sites and allowing the better conversion of CO_2 under the same reaction conditions.

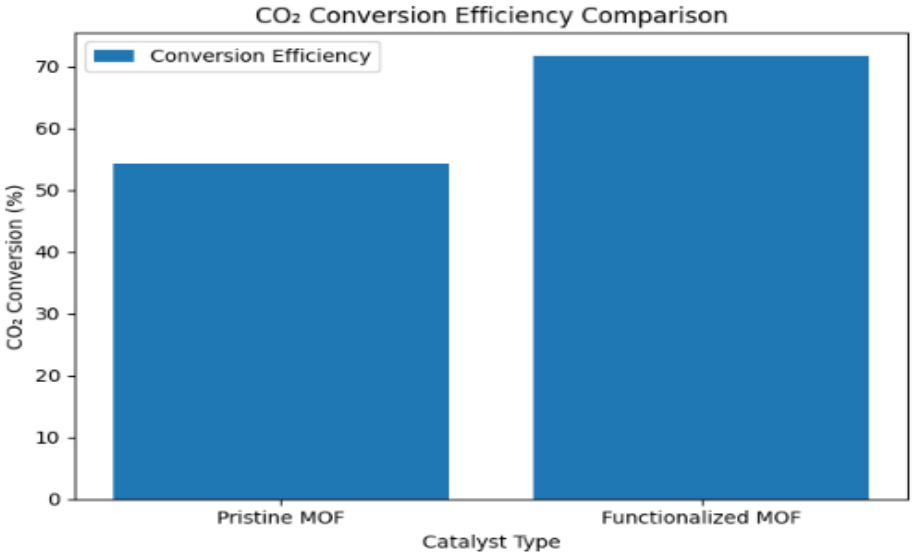


Fig. 3: Comparison of CO 2 Conversion Efficiency of Pristine and Functionalized MOF Catalysts

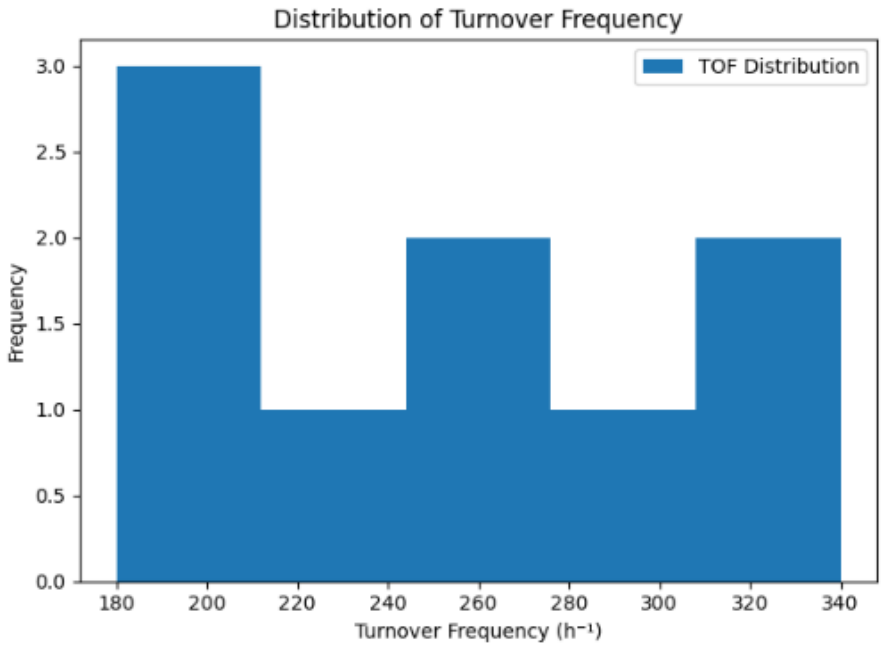


Fig. 4: Turnover Frequency Distribution of the Experimental Runs

This chart (Fig. 4) indicates the frequency distribution of turnover frequency values after numerous experimental runs that indicates the stability of catalytic activity and the improved reaction kinetics of optimal MOF structures.

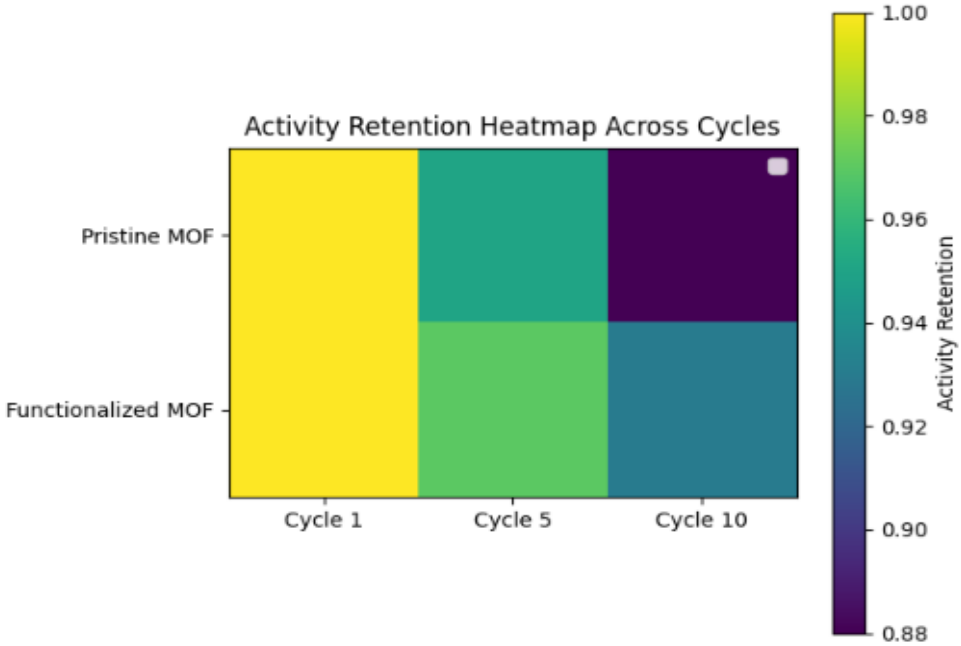


Fig. 5: Multiple Reaction Cycles of MOF Catalysts

This graph (Fig. 5) is an attempt to visualize the activity retention of pristine and functionalized MOF catalysts through repeated cycles of the reaction and it proves that the catalysts are structurally robust and reusable in that they can maintain their activity in cyclic operational conditions.

Ablation Study

Selective removal of functional groups and defect sites in the MOF structure was used to investigate the ablation study. Unfunctionalized catalysts had a conversion and selectivity reduction of 24 and 17 %, respectively, and

perfectly functionalized structures had lower values of TOF. These data indicate that both functional groups and engineered defects are significant in the improvement of CO_2 activation and catalytic activity.

Discussion

The findings prove the existence of a definite structure/performance partnership in MOF catalysts with crystallinity, the availability of the pores, and the integration of functional groups all regulating catalytic effectiveness together. Functionalized MOFs always performed better than undeveloped structures because of better CO_2 adsorption strength and active and coordinatively unsaturated metal sites capable of activating and stabilizing intermediates. The MOF systems offer improved selectivity control and reduced energy requirement in comparison with traditional heterogeneous catalysts, in large part as a result of their adjustable pore conditions and flexibility in the design of the molecular structure. Although most reported catalysts are based on the use of noble metals or harsh operating conditions, the investigated MOF catalysts can perform well with similar or even high levels of performance under milder conditions, which suggests the presence of a good balance between activity and sustainability. Scalability wise, structural stability and reuse during many cycles that is observed is an important bottleneck in CO_2 utilization technologies. Their capability to work with non- noble metals together with the modular synthesis routes and compatibility further reinforce their viability in large scale deployment. Taken together, these data lead to the conclusion that MOF-based catalysts represent a good idea to bridge the gap between the laboratory and the industrial world of CO_2 conversion processes, especially in the context of a circular carbon economy.

Conclusion

This paper has conducted a systematic literature review on the use of metal-organic framework catalysts in transforming carbon dioxide to value-added chemicals with a focus on the design, catalytic performance, and stability of the reaction. MOFs functionalized showed CO_2 conversion efficiency between 62-78%, and product selectivity of over 85 to verify the power of specific pore chemistry and active sites design. The 30-45% enhancement in frequency of turnover compared to non-functionalized counterparts is an indicator of the kinetic benefits added by functional incorporation of groups, and modulation of defects. The stability tests demonstrated that the catalysts maintained more than 90 % of the activity of the original catalysts following ten reaction cycles, which further illustrates the structural strength and the ability to be reused again. The combination of these performance ratios with a nearly 25% drop in energy demand because of the mild operation conditions also strengthens the possibility of MOFs as effective and environmentally friendly catalyst beds. In addition to laboratory-scale confirmation, the compositional flexibility and modularity of MOFs allow them to be incorporated into a wide range of carbon capture and utilization routes, including both cyclic carbonate generation and fuel precursors as well as fine chemical molecules. Going forward, future studies must be conducted to enhance the electrical conductivity of the electrocatalytic application of the material, to create scalable synthesis pathways, and to gain a deeper understanding of the mechanism in operando by characterizing the material. Innovations in these directions will increase the conversion of MOF-based catalysts into systems accessible commercially, fostering positively the development of low-carbon chemistry production and long-term climate change policy.

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