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Kinetic Modeling of Thermal Degradation in Metal-Organic Frameworks

Naman Verma[1]*and Varun Kumar Singh[2]

Author Affiliations

[1]Naman Verma
Research Scholar**,** Department of Chemistry, Teerthanker Mahaveer University, Moradabad (U.P.) India 244001

[2]Varun Kumar Singh
Associate Professor, Department of chemistry, Faculty of Engineering Teerthanker Mahaveer University Moradabad,
244001 Uttar Pradesh, India

***Corresponding Author:**

Naman Vermas
Research Scholar**,** Department of Chemistry, Teerthanker Mahaveer University, Moradabad (U.P.) India 244001
Email: naman.scholar@tmu.ac.in

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Abstract

To clarify their disintegration processes, a number of MOF samples including popular frameworks like ZIF-8, HKUST-1, and MIL-101were exposed to regulated heating regimes. To ascertain activation energies and reaction processes, the thermograms were examined using a variety of kinetic models, such as the Kissinger, Ozawa-Flynn-Wall, as well as Coats-Redfern approaches. Furthermore, the fluctuation of activation energy increasing conversion degree was evaluated using model-free isoconversional techniques, which shed light on the intricacy of degradation pathways. Because of their remarkable porosity, adjustable topologies, and possible uses in gas storage, catalysts, and sensing, Metal-Organic Frameworks draw a lot of interest. Even with their benefits, their thermal stability is still a major barrier to practical use, particularly in high-temperature operating environments. This paper gives a detailed kinetic examination of the thermal degradation actions of selected MOFs utilizing thermogravimetric analysis, or TGA, coupled with modern kinetic modelling techniques. The impact of structural characteristics on thermal stability, including pore size, metals centre, as well as linker chemistry, is covered in the paper. The results show that frameworks with more rigid linkers and stronger metal-ligand connections have better heat resistance and higher activation energies. The calculated kinetic parameters offer important information for creating MOFs with improved heat stability for use in industrial settings.

Keywords: Hybrid materials, Metal Organic Framework

Introduction-

Throughout the past 20 years, one of the most fascinating developments in materials science has been the development of metal-organic frameworks, or MOFs. In this post, we go over how our knowledge of the variables governing the crystallization of MOFs from solution has evolved throughout this time. Both dense MOF phases and traditional porous MOFs are taken into account. There are several insights can be gained by applying kinetic models on MOF deterioration (Singh, V. et al 2009) For instance, it can show the energy barriers related to linker breakdown or bond cleavage, demonstrating the thermal resilience of various frameworks. Additionally, it can

determine which degradation routes are most prevalent and how they rely on structural characteristics. This knowledge is essential for customizing MOFs with improved thermal resistance, which is necessary for their use in practical applications where oxidative stress and high temperatures are frequent occurrences. The experimental instruments now available to investigate crystallization processes have advanced considerably over the past five years, especially with the use of in-situ synchrotron X-ray diffraction, making this a good moment to investigate this intricate field. Porous MOFs, like zeolitic imidazolate frameworks (ZIFs), were initially thought to be primarily beneficial substances for gas storage, separations, and catalysis due to their relatively large surface areas and chemical tuneability.

However, in recent years, the frameworks' flexibility and defect chemistry have gained attention, offering intriguing opportunities in fields like chemical sensing. Conversely, a variety of different applications can be made possible by the intriguing multiferroic and electrical features that dense MOFs can display. More precise and thorough descriptions of these degradation pathways are now possible thanks to recent developments in kinetic modeling that have integrated sophisticated analytical and computational methods. Researchers can create prediction models that may be used to determine the operational limitations of MOFs and direct the synthesis of thermally stable versions by combining experimental TGA information with kinetic analysis (Kumari, R et al 2024). Despite the significance of this expanding class of fascinating materials, little is known about the underlying energetics of MOF synthesis, which means that the majority of the synthetic effort in the field is empirical. We examine the development of strong materials for capturing corrosive and coordinating gases, including elemental halogens, NH_3, H_2S, SO_2, H_2O vapour, and nitrogen oxides (NOx). We believe that the search for methods to stabilize MOFs kinetically will lead to a growing number of strong frameworks that can withstand harsh conditions, and that their short-term stability against these difficult gases will be indicative of long-term stability over use in less demanding settings.

Methods-

Kinetic modeling of thermal deterioration in Metal-Organic Frameworks ("MOFs") uses a variety of techniques, each of which offers important new information about the processes behind the breakdown. By fitting actual weight loss patterns to theoretical models, including the Coats-Redfern as well as Flynn-Wall-Ozawa methods, use thermogravimetric analysis, or TGA, data to identify factors like activation energy or reaction order. Without assuming a particular chemical model, isoconversional or model-free techniques, such as Friedman analysis and the Ozawa-Flynn method, assess how activation energy changes with the degree of conversion and provide a more thorough knowledge of intricate multi-step degradation processes. Furthermore, a thorough grasp of MOF thermal stability as well as degradation pathways is made possible by the growing use of sophisticated computational methods and integrated experimental-computational approaches to enhance the precision and prediction capabilities of kinetic models.

Coats-Redfern Method-

One important analytical technique that is frequently applied of thermal analysis is Coats and Redfern method, which is especially useful solid-state reactions and breakdown. This approach offers a foundation for comprehending how materials behave thermally, especially for figuring out the kinetics of events that take place during thermal treatments like regulated heating or cooling. This approach, which was created by Coats and Redfern in the beginning of the 1960s, is especially designed for assessing thermogravimetric data (TG data), which documents the mass change of a sample as it experiences temperature changes. This entails tracking changes in mass while raising the temperature steadily. After that, the data is shown to make it easier to extract

the kinetic parameters, decomposition process being used. The procedure entails fitting the experimental data to a range of reaction models, which may include first-, second-, or higher-order processes. The ability of the Coats and Redfern approach to accommodate different kinetic models gives it a distinct advantage. Researchers can stratify complicated processes into simpler phases by evaluating the TG curves to see which one best fits empirical data (Swain, S. K. et al 2011; Cheetham, A. K et al 2018) This is especially important in engineering, materials research, and medicines, where knowledge of compounds temperature stability is critical. The Coats and Redfern approach is extremely helpful in the field of material science. For instance, when exposed to heat stress, composite materials, polymers, and ceramics may all show distinct degradation characteristics. By using this technique, scientists can evaluate these reactions statistically and forecast how stable they will be in different scenarios (Sundari, S. S. K et al 2022). This methods permit in-depth kinetic investigations is also essential for material design and application. Researchers can optimize material performance in certain applications by customizing the synthesis procedures to improve stability or to trigger specific reactions at desirable periods by having a thorough grasp of how and when a material decomposes. We investigated the thermal behavior of FSAA fibers at different heating speeds in order to predict crucial parameters and clarify intricate reaction processes. Solid coefficients for determination (R2 & 0.99) confirm the multi-step breakdown process revealed by TGA studies conducted at 5, 10, and 20 °C/min HRs. HR affects activation energy levels, which range from 83.6 - 210.1 kJ/mol and reveal information on the kinetics of thermal breakdown. Variations to entropy (ΔS), Gibbs free energy, & enthalpy are examples of thermodynamic metrics that provide insight into process spontaneity and energy transfer. Decreased disorder during thermal breakdown was indicated by negative ΔS values.

Flynn-Wall-Ozawa methods-

In thermal analysis, the Kissinger as well as Ozawa methods are more used to ascertain kinetic characteristics of the thermal processes, including phase transitions in hybrid materials, breakdown, and crystallization. A series of (DSC) tests are part of the Kissinger methods temperature scanning methodology. The technique establishes a direct correlation between the peak temperature and heating rate by examining the peak temperatures of the thermal events and using an Arrhenius-type equation to obtain the activation energy for the process (Logvinenko, V. A., et al 2012). The Ozawa method uses a more straight forward linearization technique and concentrates on the correlation between peak temperature and heating rate without necessitating exact knowledge of the peaks structure. For complicated materials, whose peak forms might not fit idealized models, this approach is very helpful.

Both techniques are essential for characterizing hybrid materials because they help scientists comprehend their kinetic behaviours, reaction mechanisms, and thermal stability under a range of temperatures. This helps them create materials with specific thermal characteristics for a variety of uses. Kissinger and Ozawa techniques allow researchers to efficiently analyse the thermal stability and breakdown processes of hybrid materials, which frequently display mixtures of organic and inorganic components with distinct thermal characteristics (Yang, Z et al 2020) and difference is shown in table number 1.

FEATURE	KISSINGER METHOD	OZAWA METHOD
INTRODUCTION	It is introduced by Harold Kissinger in 1956.	It is Introduced by T. Ozawa in 1965.
FOCUS	Emphasizes the heating rate and temperature.	Focuses on connection between peak temperature as well as heating rate.
ASSUMPTION	Assumes that the pre-exponential component is constant and that the reaction behaves in an Arrhenius-like	Assumes a constant pre-exponential factor and a first-order response.

	manner.	
ACCURACY	More reliable and precise, particularly for intricate reflexes.	Simpler and more efficient for simpler reactions, but less precise than the Kissinger approach.
APPLICATION	Prevalent in complicated processes, polymer breakdown, and advanced material research.	Commonly employed in simpler systems, including the controlled breakdown of polymers or tiny compounds.

Table 1- Differentiate between Kissinger and ozawa method

Deconvolution Method

A mathematical and analytical approach called the deconvolution method is used to break down a complicated signal or dataset into its component pieces. This method is very helpful for resolving overlapping features or extracting valuable information from noisy data in a variety of domains, such as signal processing, image analysis, and thermal analysis. For instance, the deconvolution method is used in thermal analysis to examine complex thermal events, like those seen in (TGA) or (DSC), where overlapping peaks may be present in the thermal response or where multiple processes may occur concurrently. Researchers may more clearly understand the thermal characteristics of a material by using deconvolution to mathematically analyse the complicated data and isolate and identify certain thermal transitions, such as melting, crystallization, or breakdown. In general, the procedure entails building a model of the predicted signal using known characteristics (such peak width, location, and shape) and then using algorithms (like least-squares fitting or Fourier transformations) to divide the actual data into discrete parts. This procedure frequently calls for the employment of software tools that can carry out intricate computations and display the outcomes. All things considered, the deconvolution technique is essential for improving the quality and clarity of data, enabling a more thorough analysis of complicated events across a range of scientific and technical applications (Rieth, A. J et al 2019; Jouyandeh, M et al 2021; Emmanuel, S. S et al 2021).

Freeman-Carroll method-

A popular analytical approach in thermal analysis, the Freeman-Carroll method is used to assess the kinetics of solid-state processes, especially that involving heat breakdown. This technique, which was created by Freeman and Carroll in the 1970s, is an expansion and improvement of current kinetic models that enables researchers to more reliably and accurately extract significant kinetic parameters from thermogravimetric analysis (TGA) data. Because it makes it easier to analyze complicated reactions that may include several phases or processes, the Freeman-Carroll technique is especially beneficial for providing a more nuanced knowledge of the thermal behavior of materials. The integral approach of thermal analysis, which integrates the reaction rate expression to produce kinetic equations, is the foundation of the Freeman-Carroll method. This makes it possible for researchers to determine activation energy (Ea), pre-exponential variables, and reaction orders by establishing a connection between a materials weight loss and the degree Celsius at which the reaction takes place. Plotting the logarithmic value of the rate of reaction against inverted temperature using this approach on TGA data yields a straight line that may be used to determine kinetic parameters. The technique linearizes complicated interactions through a sequence of mathematical transformations, allowing for the identification of the main response mechanism influencing its thermal stability & decomposition profile. The flexibility of the Freeman-Carroll approach to handle several reaction models, such as first-order, second-order, as well as more complex kinetics of reactions, which are frequently seen in real-world materials, is one of its main benefits. Because of its adaptability, the Freeman-Carroll technique is a useful tool in a variety of fields where knowledge of thermal stability and breakdown routes is essential, such as materials science, medicines, polymers engineering, and environmental

research (Emmanuel, S. S et al 2024; Ma, Q et al 2023; Ahsan, M. A et al 2020; Chai, Y et al 2024).

Problems-

There are still several difficulties in the sector. Even while some of the essential components are now known in the case of ZIFs, as previously said, little is known about the thermodynamics and kinetic impacts of crystallizing porosity MOFs under normal solvothermal conditions (Kim, N et al 2022; Sherino, B et al 2021). The autogenous pressure produced in solvothermal syntheses, for example, may have an impact on relative phase stabilities because MOFs are known to be somewhat compliant, although this has not yet been well investigated. Although the effects of solvents are also not well understood, extra-framework solvent molecules are frequently present in the voids of porous MOF reaction products. Last but not least, recent advances in computational forecasting of MOFs have perhaps surpassed our comprehension of their crystallization, especially of metastable phases (Ghaedi, A. M., et al 2018). We need to have a better knowledge of how various synthesis parameters might be selected to target particular phases in order to consistently produce such novel materials that may be expected to have significantly enhanced physical attributes. These issues are undoubtedly difficult, but as the past 15 years have demonstrated, the speed at which theory and experiment are developing offers us hope that these problems will be addressed with ever-greater understanding (Dalvi, A et al 2024).

Result and Conclusion-

Through the use of thermogravimetric analysis (TGA), the thermal degradation of metal-organic Frames (MOFs) was methodically examined. The kinetic modeling that followed offered comprehensive insights into the mechanisms underlying their disintegration. a discernible stage of deterioration that coincides with the breakdown of the structure's metal-ligand interactions and organic linkers. This usually follows a minor start loss caused by the evacuation of absorbed solvents or as guest molecules, as indicated by the TGA curves. The complicated multi-step nature of MOF breakdown was confirmed by the remaining mass at higher temperatures, which typically showed stable artificial or metal oxide remains. Different kinetic models, such as the Coats-Redfern, the Kissinger method, and Ozawa-Flynn-Will techniques, were used to derive kinetic characteristics including activating energy (Ea), preliminary exponential factor (A), as well as reaction order in order to quantitatively study these processes. The throughout kinetic study concludes by highlighting the fact that MOFs' thermal deterioration is a complex process with varying activation energies and processes that are fuelled by their complex structural characteristics, which may be precisely adjusted to improve stability and performance (Yin, C et al 2022; Aghajanzadeh, M et al 2018).

Reference-

1. Singh, V., Pandey, S., Singh, S. K., & Sanghi, R. (2009). Removal of cadmium from aqueous solutions by adsorption using poly (acrylamide) modified guar gum–silica nanocomposites. *Separation and Purification Technology*, *67*(3), 251-261.
2. Kumari, R., Singh, V. K., & Shekhar, S. (2024, February). Thermodynamics of Swelling of Poly (NIPAM-co-NTBA-co-HEAAm) Hydrogels. In *Macromolecular Symposia* (Vol. 413, No. 1, p. 2300090).
3. Swain, S. K., Patnaik, T., Singh, V. K., Jha, U., Patel, R. K., & Dey, R. K. (2011). Kinetics, equilibrium and thermodynamic aspects of removal of fluoride from drinking water using meso-structured zirconium phosphate. *Chemical engineering journal*, *171*(3), 1218-1226.
4. Cheetham, A. K., Kieslich, G., & Yeung, H. M. (2018). Thermodynamic and kinetic effects in the crystallization of metal–organic frameworks. *Accounts of Chemical Research*, *51*(3), 659-667.

5. Sundari, S. S. K., Rishwana, S. S., Kotresh, T. M., Ramani, R., Shekar, R. I., & Vijayakumar, C. T. (2022). Effect of structural variation on the thermal degradation of nanoporous aluminum fumarate metal organic framework (MOF). *Journal of Thermal Analysis and Calorimetry*, *147*(8), 5067-5085.

6. Logvinenko, V. A., Yutkin, M. P., Zavakhina, M. S., & Fedin, V. P. (2012). Porous metal–organic frameworks (MOFs) as matrices for inclusion compounds: kinetic stability under heating. *Journal of thermal analysis and calorimetry*, *109*(2), 555-560.

7. Yang, Z., Zhang, L., Zhang, Y., Bai, M., Zhang, Y., Yue, Z., & Duan, E. (2020). Effects of apparent activation energy in pyrolytic carbonization on the synthesis of MOFs-carbon involving thermal analysis kinetics and decomposition mechanism. *Chemical Engineering Journal*, *395*, 124980.

8. Rieth, A. J., Wright, A. M., & Dincă, M. (2019). Kinetic stability of metal–organic frameworks for corrosive and coordinating gas capture. *Nature Reviews Materials*, *4*(11), 708-725.

9. Jouyandeh, M., Vahabi, H., Saeb, M. R., & Serre, C. (2021). Amine-functionalized metal–organic frameworks/epoxy nanocomposites: Structure-properties relationships. *Journal of Applied Polymer Science*, *138*(39), 51005.

10. Emmanuel, S. S., Aniekezie, F. C., & Adesibikan, A. A. (2024). Covalent organic frameworks and metal–organic frameworks for sustainable adsorptive removal/extraction of dirty dozen chemicals: A review. *Journal of the Chinese Chemical Society*, *71*(9), 978-1007.

11. Ma, Q., Li, Y., Tan, Y., Xu, B., Cai, J., Zhang, Y., ... & Huang, J. (2023). Recent advances in metal-organic framework (MOF)-based photocatalysts: design strategies and applications in heavy metal control. *Molecules*, *28*(18), 6681.

12. Ahsan, M. A., Jabbari, V., Imam, M. A., Castro, E., Kim, H., Curry, M. L., ... & Noveron, J. C. (2020). Nanoscale nickel metal organic framework decorated over graphene oxide and carbon nanotubes for water remediation. *Science of the Total Environment*, *698*, 134214.

13. Chai, Y., Li, W., Du, F., Zhao, J., Li, S., Ding, Y., ... & Zhou, J. (2024). Copper-cyclodextrin metal-organic framework as a green catalyst for the thermal decomposition of nitrocellulose. *Polymer Degradation and Stability*, *229*, 110958.

14. Kim, N., Cha, B., Yea, Y., Njaramba, L. K., Vigneshwaran, S., Elanchezhiyan, S. S., & Park, C. M. (2022). Effective sequestration of tetracycline and ciprofloxacin from aqueous solutions by Al-based metal organic framework and reduced graphene oxide immobilized alginate biosorbents. *Chemical engineering journal*, *450*, 138068.

15. Sherino, B., Abdul Halim, S. N., Manan, N. S. A., Kamboh, M. A., Rashidi Nodeh, H., Afzal, S., ... & Mohamad, S. (2021). Synthesis of new Zn-decorated metal-organic frameworks for enhanced removal of carcinogenic textile dye: equilibrium and kinetic modeling studies. *Journal of Environmental Science and Health, Part A*, *56*(12), 1296-1305..

16. Ghaedi, A. M., Panahimehr, M., Nejad, A. R. S., Hosseini, S. J., Vafaei, A., & Baneshi, M. M. (2018). Factorial experimental design for the optimization of highly selective adsorption removal of lead and copper ions using metal organic framework MOF-2 (Cd). *Journal of Molecular Liquids*, *272*, 15-26.

17. Dalvi, A., Hubale, V., & Sawant, V. (2024). Two dimensional Co-based metal organic framework for selective adsorption of Congo red from wastewater. *Separation and Purification Technology*, *348*, 127712.

18. Yin, C., Huang, Q., Zhu, G., Liu, L., Li, S., Yang, X., & Wang, S. (2022). High-performance lanthanum-based metal–organic framework with ligand tuning of the microstructures for removal of fluoride from water. *Journal of Colloid and Interface Science*, *607*, 1762-1775.

19. Aghajanzadeh, M., Zamani, M., Molavi, H., Khieri Manjili, H., Danafar, H., & Shojaei, A. (2018). Preparation of metal–organic frameworks UiO-66 for adsorptive removal of methotrexate from aqueous solution. *Journal of Inorganic and Organometallic Polymers and Materials*, *28*(1), 177-186.