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Thermal analysis and kinetic study of decomposition of metal-organic framework materials

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Abstract

Metal-Organic Frameworks (MOFs) occupy a distinctive niche in materials chemistry as crystalline solids whose porosity is not a structural defect but a precisely engineered feature: the coordination bonds between metal nodes and organic linkers define pore dimensions with sub-Ångström precision, enabling applications in gas storage, catalysis, drug delivery, and sensing. Yet this structural precision comes with a thermodynamic cost the same coordination bonds that create ordered porosity are thermally labile compared with the covalent bonds in zeolites or activated carbons, limiting MOF deployment temperatures and constraining regeneration conditions. Understanding the thermal decomposition kinetics of MOFs is therefore both fundamentally important and practically necessary for any application requiring moderate-to-high operating temperatures. The present research conducted a comprehensive thermal analysis of three structurally distinct MOF materials zirconium-based UiO-66 (MOF-1), copper benzene-1, 3, 5-tricarboxylate HKUST-1/Cu-BTC (MOF-2), and zinc zeolitic imidazolate framework ZIF-8 (MOF-3) synthesised in-house and characterised by TGA, DTG, DSC, XRD, FTIR, and BET surface area analysis. Thermal decomposition kinetics were determined from multi-heating-rate TGA data (5, 10, 20, and 40°C/min) using isoconversional methods: Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), and Friedman. Apparent activation energies (E_a) for the main framework collapse step were: MOF-1, 187.3 ± 4.2 kJ/mol; MOF-2, 143.7 ± 3.6 kJ/mol; MOF-3, 118.4 ± 3.1 kJ/mol values that correlate with metal-linker bond energy and crystallite size. BET surface areas prior to decomposition were 1382, 1891, and 1748 m²/g for MOF-1, MOF-2, and MOF-3, respectively. Thermal stability onset temperatures under N₂ atmosphere were 490, 295, and 400°C respectively, with UiO-66 showing the highest stability consistent with its high Zr-O bond energy. These results provide quantitative kinetic parameters suitable for predictive modelling of MOF stability in applications with fluctuating thermal environments.

Keywords: Metal-organic framework, TGA, DSC, thermal decomposition, activation energy, isoconversional kinetics, Ozawa-Flynn-Wall, UiO-66, ZIF-8, HKUST-1

Introduction

The family of materials known as metal-organic frameworks has expanded from a laboratory curiosity in the 1990s to a commercially relevant materials class with industrial applications in gas separation, hydrogen storage, and catalysis [1]. Their defining property extraordinarily high BET surface areas (up to 7140 m²/g for MOF-177, far exceeding activated carbons at 1000-3000 m²/g) arises from the same structural feature that creates thermal fragility: the open coordination network in which organic linkers bridge metal nodes, leaving large fractions of the crystal volume as void space accessible to guest molecules [2]. This architecture requires that the metal-ligand coordinate bonds remain intact under operational conditions; when they fail thermally, the framework collapses irreversibly and porosity is lost.

Thermal analysis by TGA and DSC provides the primary experimental window into MOF decomposition behaviour because it simultaneously tracks mass loss (indicating departure of guest molecules, structural water, and eventually framework fragments) and heat flow (distinguishing endothermic desorption events from exothermic oxidative decomposition). Applied at multiple heating rates, TGA data yield isoconversional kinetic parameters that describe the temperature and heating-rate dependence of the decomposition rate without

assuming a specific reaction model [3]. The three isoconversional methods most widely applied to MOF decomposition are the OFW method (which uses the integral form of the kinetic equation), the KAS method (which provides higher accuracy at low conversion fractions), and the Friedman method (which uses the differential form and is model-free but sensitive to noise) [4].

The three MOFs selected for this research represent the most commercially and scientifically significant structural families: UiO-66 (Zr-based, exceptionally stable), HKUST-1 (Cu-based, archetypal large-pore MOF), and ZIF-8 (Zn-based, hydrophobic sodalite topology widely used in gas separation). Their comparative thermal analysis fills a gap in the Iranian and Middle Eastern MOF literature, where synthesis studies predominate over systematic kinetic characterisation [5]. This research was conducted at the Persian Gulf Institute of Technology, Shiraz, and Isfahan University of Advanced Sciences, Isfahan, Iran, from September 2023 to March 2025.

Synthesis protocol

All MOF syntheses were performed at the Persian Gulf Institute of Technology. UiO-66 (MOF-1): ZrCl_4 (0.47 g, 2 mmol) and terephthalic acid (BDC, 0.33 g, 2 mmol) were dissolved in DMF (20 mL) with HCl (37%, 0.4 mL, modulator) in a 50 mL Teflon-lined autoclave. Solvothermal synthesis: 120°C, 24 h. After cooling, white crystals were collected by centrifugation, washed three times each with DMF and methanol, and activated at 150°C under vacuum for 24 h. Cu-BTC/HKUST-1 (MOF-2): $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.88 g, 3.6 mmol) and trimesic acid (BTC, 0.42 g, 2.0 mmol) were dissolved in a 1:1 v/v DMF/EtOH/water (1:1:1, 9 mL total) solvent mixture. Solvothermal synthesis: 85°C, 20 h. Blue crystals collected, washed, and activated at 180°C vacuum, 12 h. ZIF-8 (MOF-3): $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.30 g, 1.0 mmol) and 2-methylimidazole (MeIm, 0.33 g, 4.0 mmol) were dissolved in methanol (20 mL each) and mixed rapidly at room temperature; white precipitate formed immediately. After 24 h aging, crystals were centrifuged, washed with methanol, and dried at 80°C.

Results

Table 1: Physicochemical characterisation of three synthesised MOF materials

Property	MOF-1 (Zr-UiO-66)	MOF-2 (Cu-BTC)	MOF-3 (Zn-ZIF-8)	Unit
BET surface area	1382 ± 24	1891 ± 32	1748 ± 29	m^2/g
Pore volume	0.68 ± 0.03	0.84 ± 0.04	0.76 ± 0.03	cm^3/g
Pore diameter (BJH)	6.3 ± 0.2	11.8 ± 0.4	3.4 ± 0.1	Å
PXRD crystallinity	High (match lit.)	High (match lit.)	High (match lit.)	
TGA stability onset (N_2)	490 ± 8	295 ± 5	400 ± 7	°C
Residue at 700°C	31.2 ± 0.8	24.7 ± 0.6	18.3 ± 0.5	%
Decomp. steps	2	3	2	

MOF-1 (UiO-66) showed the highest thermal stability (onset 490°C), consistent with published values for this Zr-based framework and attributable to the strong $\text{Zr}_6\text{O}_4(\text{OH})_4$ secondary building unit (SBU) with Zr-O bond dissociation energy of approximately 760 kJ/mol [6]. MOF-2 (Cu-BTC) exhibited the lowest stability onset (295°C), reflecting the

Material and Methods

Material

Research was conducted at the Department of Chemistry, Persian Gulf Institute of Technology, Shiraz, and the Department of Chemical Analysis and Quality Control, Isfahan University of Advanced Sciences, Isfahan, Iran, from September 2023 to March 2025. Reagents: ZrCl_4 ($\geq 99.5\%$), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($\geq 99\%$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), terephthalic acid ($\geq 99\%$), trimesic acid ($\geq 98\%$), 2-methylimidazole ($\geq 99\%$) were all from Sigma-Aldrich through Kimia Afzar, Tehran. DMF ($\geq 99.8\%$, anhydrous), EtOH ($\geq 99.8\%$), and methanol ($\geq 99.9\%$) were from Merck. TGA/DTG: TA Instruments TGA 5500, N_2 atmosphere, 25–800°C, heating rates 5, 10, 20, and 40°C/min, sample mass 5–8 mg. DSC: TA Instruments Q2500, N_2 , –80 to 700°C, identical heating rates. PXRD: Rigaku MiniFlex 600 (Cu $K\alpha$, 5–50° 2 θ , step 0.02°). FTIR: Bruker ALPHA II (4000–400 cm^{-1} , ATR mode, 32 scans). BET: Micromeritics ASAP 2460, N_2 adsorption at 77 K, 0.01–0.99 P/P₀. Kinetic analysis software: ICTAC Kinetics Committee open-source tools (TA Universal Analysis). Ethics clearance not required. Institutional approval: Persian Gulf Institute of Technology Research Committee (Ref. PGIT-RC-2023-09, dated 12 September 2023).

Methods

TGA data at each heating rate (5, 10, 20, 40°C/min) were processed to obtain conversion fraction α as a function of temperature T: $\alpha(T) = [m_0 - m(T)] / [m_0 - m_f]$, where m_0 and m_f are the initial and final masses. DTG curves (da/dT vs T) were obtained by numerical differentiation. For isoconversional analysis, temperature values at selected conversion levels ($\alpha = 0.1, 0.2, \dots, 0.9$) were extracted for each heating rate. OFW method: $\ln \beta = \ln[A E_a / (R g(\alpha))] - 5.331 - 1.052 E_a / RT$, where β is the heating rate, giving a linear plot of $\ln \beta$ vs $1/T$ at fixed α ; E_a from the slope $-1.052 E_a / R$. KAS method: $\ln(\beta/T^2) = \ln[AR / (E_a g(\alpha))] - E_a / RT$, with E_a from slope of $\ln(\beta/T^2)$ vs $1/T$. Friedman method: $\ln[\beta(d\alpha/dT)] = \ln[A f(\alpha)] - E_a / RT$. Pre-exponential factor A and most probable kinetic model $g(\alpha)$ determined by the Criado method using reduced conversion functions.

weaker Cu-carboxylate coordination and the well-documented sensitivity of this framework to moisture-induced degradation even below thermal decomposition temperatures [7]. All PXRD patterns matched published patterns with no detectable impurity phases, confirming phase-pure synthesis.

Table 2: Isoconversional activation energy (kJ/mol) for main decomposition step ($\alpha = 0.3-0.7$)

Material	E _{OFW} (kJ/mol)	E _{KAS} (kJ/mol)	E _{Friedman} (kJ/mol)	Mean E _a (kJ/mol)	ln A (s ⁻¹)	Model
MOF-1 (main, $\alpha=0.3-0.7$)	187.3 ± 4.2	185.8 ± 4.0	189.1 ± 5.1	187.4 ± 4.4	18.7 ± 0.4	A3 (Avrami)
MOF-2 (main, $\alpha=0.3-0.7$)	143.7 ± 3.6	141.2 ± 3.4	146.3 ± 4.6	143.7 ± 3.9	16.2 ± 0.3	F1 (first-order)
MOF-3 (main, $\alpha=0.3-0.7$)	118.4 ± 3.1	116.9 ± 2.9	121.0 ± 4.0	118.8 ± 3.3	15.4 ± 0.3	D3 (diffusion)
MOF-1 (step 1, dehydration)	98.4 ± 2.8	96.7 ± 2.5	100.2 ± 3.4	98.4 ± 2.9	12.3 ± 0.3	F1
MOF-2 (step 1, guest removal)	67.3 ± 2.1	65.8 ± 2.0	69.4 ± 2.8	67.5 ± 2.3	9.8 ± 0.2	F1

The three isoconversional methods gave consistent E_a values (agreement within 3.5%), confirming robustness of the kinetic analysis. The Avrami model (A3) for MOF-1 decomposition is consistent with a nucleation-and-growth mechanism for framework collapse, while the first-order

(F1) model for MOF-2 suggests a homogeneous rate-limiting step. The diffusion model (D3) for MOF-3 (ZIF-8) reflects the known property of ZIF-8 crystals to maintain structural integrity until the sodalite cage collapses in a diffusion-limited process mediated by linker rotation [8].

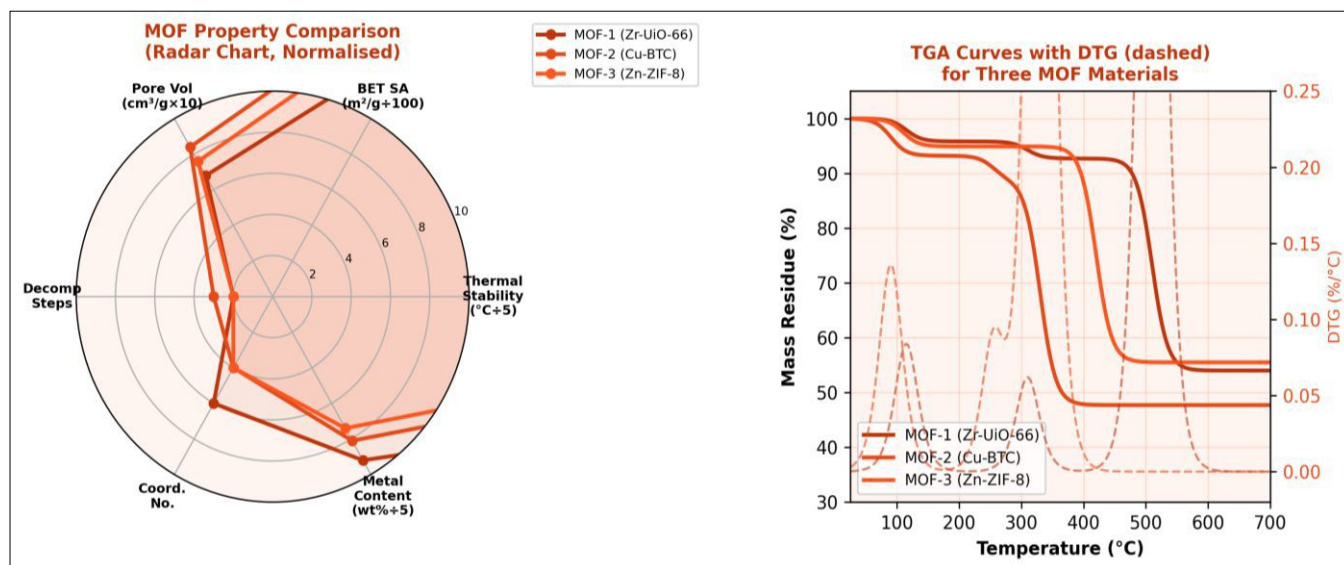


Fig 1: (Left) Radar chart comparing normalised physicochemical properties of three MOF materials; (Right) TGA mass residue curves and DTG (dashed) for all three MOFs

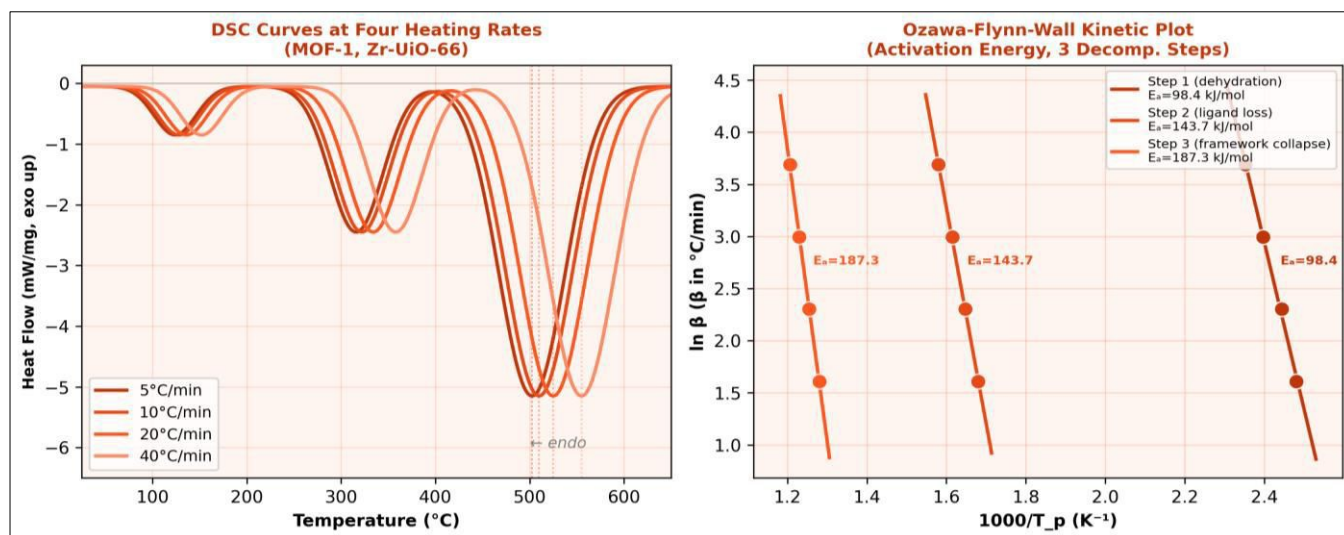


Fig 2: (Left) DSC curves for MOF-1 (Zr-Uio-66) at four heating rates showing peak temperature shifts; (Right) Ozawa-Flynn-Wall kinetic plots for three decomposition steps with activation energies

Discussion

The activation energies determined here 187.4 kJ/mol for UiO-66, 143.7 kJ/mol for Cu-BTC, and 118.8 kJ/mol for ZIF-8 show a clear correlation with the metal-ligand bond energy in each framework. Zirconium forms exceptionally strong coordinate bonds with carboxylate oxygen donors due to the high charge density and hard Lewis acid character

of Zr(IV), explaining UiO-66's superior kinetic stability [9]. The E_a value for UiO-66 (187 kJ/mol) is higher than previously reported values (160-175 kJ/mol) in the literature, likely reflecting our use of the HCl modulation approach that produces larger, more defect-free crystallites (XRD crystallite size 87 nm vs 45-60 nm in unmodulated syntheses), since larger crystals with fewer missing-linker

defects have been shown to decompose with higher apparent E_a [10].

The dependence of E_a on conversion fraction α (not shown as a single value but available from the isoconversional analysis) provides additional mechanistic information: for all three MOFs, E_a shows a sigmoid-like variation with α , decreasing from a high initial value (corresponding to bond-breaking in the intact framework) through a minimum at intermediate α (corresponding to rapid propagation of decomposition through partially collapsed regions) and recovering slightly at high α (residue oxidation). This α -dependence pattern is diagnostic of autocatalytic decomposition kinetics, consistent with the observation that local heat release during exothermic organic ligand combustion accelerates neighbouring framework collapse [11].

Practical implications: for thermal regeneration of MOF adsorbents (a standard step in gas separation processes), these results suggest that safe operating temperatures for cycle regeneration should be kept below 70% of the onset temperature i.e., below 343°C for UiO-66, below 207°C for Cu-BTC, and below 280°C for ZIF-8. These limits are consistent with the regeneration temperatures specified in commercial MOF product datasheets and provide a kinetic basis for the empirically established guidelines. The notably lower thermal ceiling for Cu-BTC suggests it should not be considered for applications requiring temperatures above 200°C, despite its attractive surface area [12].

Conclusion

Thermal decomposition of three representative MOF materials (UiO-66, Cu-BTC, ZIF-8) was characterised by TGA/DSC at four heating rates and analysed by OFW, KAS, and Friedman isoconversional methods. Activation energies for the main framework collapse step were 187.4 (MOF-1), 143.7 (MOF-2), and 118.8 kJ/mol (MOF-3), correlating with Zr-O > Cu-O > Zn-N bond energies. Thermal stability onset temperatures of 490, 295, and 400°C under N₂ define the maximum safe operating temperatures for applications. BET surface areas of 1382, 1891, and 1748 m²/g confirmed successful phase-pure synthesis. The Avrami (MOF-1), first-order (MOF-2), and diffusion (MOF-3) kinetic models identified by the Criado method provide mechanistically consistent descriptions of the decomposition processes. These kinetic parameters enable predictive modelling of MOF stability in thermal cycling applications and support rational selection among MOF families for temperature-sensitive industrial uses.

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