

Non-isothermal decomposition kinetics of copper benzene tricarboxylate metal organic framework

I. Joshi¹, V. Rani², P. Joshi³, K. Khati¹, S. Mehtab¹, M.G.H. Zaidi^{1*}, P.K. Roy⁴

¹Department of Chemistry, G.B.Pant University of Agriculture and Technology, Pantnagar, Uttarakhand-263145, India

²Department of Physics, Sri Ram Singh Dhoni Government Degree College Janti, Uttarakhand-263626, India

³Department of Chemistry, School of Allied Sciences, Dev Bhoomi Uttarakhand University, Naugaon-248007, India

⁴Centre for Fire, Explosive and Environment Safety, Defence Research Development Organisation, Timarpur, Delhi-110054, India

Received: March 15, 2023; Revised: March 30, 2023

The thermal decomposition of copper benzene tricarboxylate metal organic framework (HKUST-1) was studied by dynamic thermogravimetry. The decomposition proceeds *via* a single step and corresponding data was examined using various mathematical models. The Coats-Redfern (C-R) and Horowitz-Metzger (H-M) methods were used to compute the kinetic and thermodynamic parameters, including frequency factor (A), activation energy (E_a), change in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The mechanism of the degradation follows the non-evoking equation for three-quarters order mechanism (F_{3/4}), for which $[g(\alpha)=1 - (1 - \alpha)^{1/4}]$ and the rate-controlling method are the consequences of the chemical process. According to the C-R approach, E_a (KJ/mol), ΔH (KJ/mol), ΔS (KJ/mol-K) and ΔG (KJ/mol) for F_{3/4} mechanism were 67.27, 61.92, -0.16 and 166.17, which are in close agreement with values determined by the H-M method, 67.30, 62.20, -0.26, 219.00, respectively. A (min⁻¹) provides considerably different values from both methods.

Keywords: Copper benzene tricarboxylate, Metal-organic frameworks, Non-isothermal kinetics, Thermal and kinetic parameters.

INTRODUCTION

The term “metal-organic frameworks” (MOFs) refers to unique functional materials made up of periodic spatial or planar arrangements of metal ions that are covalently bound to organic ligands. In the framework, the metal cluster serves as “lateral” and organic ligands act as “joint”. MOFs have gained popularity in recent years as one of the most developed and used porous materials. Therefore, several scientists have synthesized a variety of porous materials with specialized properties and requirements based on their intended use such as highly efficient adsorbents [1], thin film devices [2], catalysts [3], and gas-storage materials [4]. MOFs are employed in a wide range of applications, including compound separation [5], sensors [6], supercapacitors [7] and particularly for selective adsorption and degradation [8]. This is due to their sizeable surface area, high and tunable porosity and accessibility of active sites [3]. The adjustable methods of synthesis, designs, and morphologies of numerous kinds of MOFs are fascinating research topics in electrochemical analysis such as oxidation of tiny molecules like nitrite [9], ethanol [10] and glucose, as well as reduction of hydrogen peroxide [11]. The stability of the MOFs should be one of the most important criteria for real-world applications.

For instance, stability of MOF offers ample potential for fluorescence sensing [12], photocatalysis [13], drug delivery [14] and enzyme immobilization [15]. Therefore, MOFs stability must be ensured when they are utilised for specific applications in order to keep the desired functionalities and features. The three foremost kinds of stabilities are chemical, thermal and mechanical stability. However, it is crucial to consider that chemical and thermal stability are closely associated with each other. Heating often has the ability to change the chemical structure of MOFs by starting or accelerating the chemical reaction. This causes the associated framework to collapse by rupturing the metal-ligand coordination linkage, or occasionally it can also have an impact on the organic ligand itself [16]. Chemical and thermal stabilities are vital for catalytic operations [17], while mechanical stability is important for structuring MOF, such as creating pellets or other compressed shapes [18]. Chemical stability is also crucial for applications like molecule separation and drug delivery [19].

Thermally stable materials like polymers [20] and their composites [21] are highly prized and necessary for industrial applications. A MOF is said to be thermally stable if it can be heated to a relatively high temperature without experiencing

* To whom all correspondence should be sent:
E-mail: mghzaidi@yahoo.com

permanent changes to its chemical and physical composition [16]. When MOFs are subjected to heat treatment, they can degrade in a variety of ways including amorphization [22], graphitization [23], melting [24], and metal-oxo-cluster dehydration [25]. Therefore, thermogravimetric (TG), differential thermal analysis (DTA) and derivative thermogravimetric (DTG) techniques are employed to gauge the thermal stability of MOFs [26]. Thermal analysis can be used to identify characteristics such as composition, transition temperature, purity, stability, thermal expansion, loss of modulus, and energy dissipation [27].

Copper (Cu)-based MOFs, i.e., copper benzene tricarboxylate MOF are one type of MOFs that is still being extensively explored due to exceptional physical and chemical properties. HKUST-1 (Hong Kong University of Science and Technology-1) is unquestionably one of the most researched and quoted MOFs also known as MOF-199. HKUST-1 is composed of Cu₂ paddle-wheel clusters connected with benzene-1,3,5-tricarboxylic acid to form a

three-dimensional porous network having the chemical formula [Cu₃(BTC)₂(H₂O)₃]_n. [28].

The current study aims to estimate the kinetic and thermodynamic parameters of solid-state decomposition of HKUST-1 using TG data. All metrics for HKUST-1 were analysed using the Coats and Redfern (C-R) and Horowitz and Metzger (H-M) techniques, including activation energy (E_a), frequency factor (A), change in enthalpy (ΔH), change in entropy (ΔS), and change in Gibbs free energy (ΔG).

EXPERIMENTAL

Materials and measurement

HKUST-1 was procured from the Centre of Fire, Explosives and Environment Safety Lab, Defense research Development Organization Delhi. The thermogravimetric measurement was carried out in air at a flow rate of 200 ml/min in the temperature range of 35°C-1000°C using EXSTAR TG/DTA 6300. For the experiment 10.34 mg sample weight was used at a heating rate of 10° C/min.

Table 1. Algebraic expressions for g(α) and its corresponding mechanism.

Symbol	g(α)	Rate determining process
Acceleratory rate equations		
P _{1/2}	α ^{1/2}	Nucleation
P _{1/3}	α ^{1/3}	Nucleation
P _{1/4}	α ^{1/4}	Nucleation
P _{3/2}	α ^{3/2}	Nucleation
Non evoking equations		
F _{1/3}	1 - (1-α) ^{2/3}	Chemical reaction
F _{3/4}	1 - (1-α) ^{1/4}	Chemical reaction
F _{3/2}	1/(1-α) ^{1/2} - 1	Chemical reaction
F ₂	1/(1-α) - 1	Chemical reaction
F ₃	1/(1-α) ² - 1	Chemical reaction
Deceleratory rate equations		
F ₀ , P ₁ , R ₁	α	Contracting disk
F _{1/2} , R ₂	1-(1-α) ^{1/2}	Contracting cylinder
F _{2/3} , R ₃	1-(1-α) ^{1/3}	Contracting spherical
D ₁	α ²	One-dimensional diffusion
D ₂	α + (1-α)ln(1-α)	Two-dimensional diffusion
D ₃	[1 - (1-α) ^{1/3}] ²	Three-dimensional diffusion (spherically)
D ₄	(1 - 2α/3) - (1 - α) ^{2/3}	Three-dimensional diffusion (cylindrically)
Sigmoidal rate equation		
A ₁ , F ₁	-ln(1-α)	Nucleation and growth, n=1
A _{3/2}	[-ln(1-α)] ^{2/3}	Nucleation and growth, n=1.5
A ₂	[-ln(1-α)] ^{1/2}	Nucleation and growth, n=2
A ₃	[-ln(1-α)] ^{1/3}	Nucleation and growth, n=3
A ₄	[-ln(1-α)] ^{1/4}	Nucleation and growth, n=4

Integral methods

The integral function $g(\alpha)$ dictated by the conversion process and the mathematical model for the most common solid-state reaction processes are shown in Table 1 [29, 30].

For the current study, two integral approaches were employed. One calculation strategy was based on the C-R method, and the other was based on the H-M method [31-33].

RESULTS AND DISCUSSION

Thermogravimetric analysis

Fig. 1. depicts the thermal degradation curve of HKUST-1 under air corresponding to dynamic TG-DTA-DTG experiment performed at a heating rate of 10°C/min. Before the decomposition, the temperature-dependent weight loss curve shows almost 25% losses from 30 to 137°C due to exclusion of residual solvents and guest molecules that are contaminated with HKUST-1. The subsequent weight loss of 4.2% at 137 to 280°C indicates loss of water molecules coordinated to Cu. It is evident that at high temperatures, coordinate bonds break rather than solvent is freed from the pores of MOFs [34]. The decomposition of HKUST-1 appeared in the temperature range from 286 to 380°C, leaving 26% weight residue (Fig. 1a). This was associated with an intense DTA signal at 0.599 mV with peak temperature of 373°C. DTA reveals exothermic decomposition of HKUST-1 with -4.20 J/mg of heat of fusion. Decomposition of HKUST-1 terminated at 548°C, leaving 27.7% char residue. Further, fusion of HKUST-1 was observed at DTG peak temperature of 304°C with 7.2 mg/min (Fig. 1b).

Calculation of thermodynamic parameters from TGA

To calculate activation energy for the single-step decomposition of HKUST-1, first C-R equation [30] was used:

$$\ln g(\alpha) = \ln\left(\frac{ART^2}{\beta Ea}\right) - \frac{Ea}{RT}$$

A plot of $\ln g(\alpha)$ vs $1000/T$ can be used to calculate the activation energy for each of the degradation processes described in Table 1. Table 2, shows activation energy and correlations for different mechanisms. Analysis of this table confirms that solid state thermo degradation mechanism may follow non evoking equation of three-quarter order ($F_{3/4}$) or decelerator rate equation following power law, i.e. ($F_{2/3}$) and Jander equation i.e. (D_3) (Fig. 1c). The E_a for the $F_{3/4}$ mechanism is 67.27KJ/mol, with a correlation value of 0.99613. The $F_{2/3}$ shows 62.72 and D_3 was found to be 125.44 KJ/mol, having almost the same correlation value.

All the thermodynamic parameters for these three mechanisms are described in Table 3. In order to confirm the exact degradation mechanism, we have also calculated activation energy and other thermodynamic parameters using the H-M equation [30].

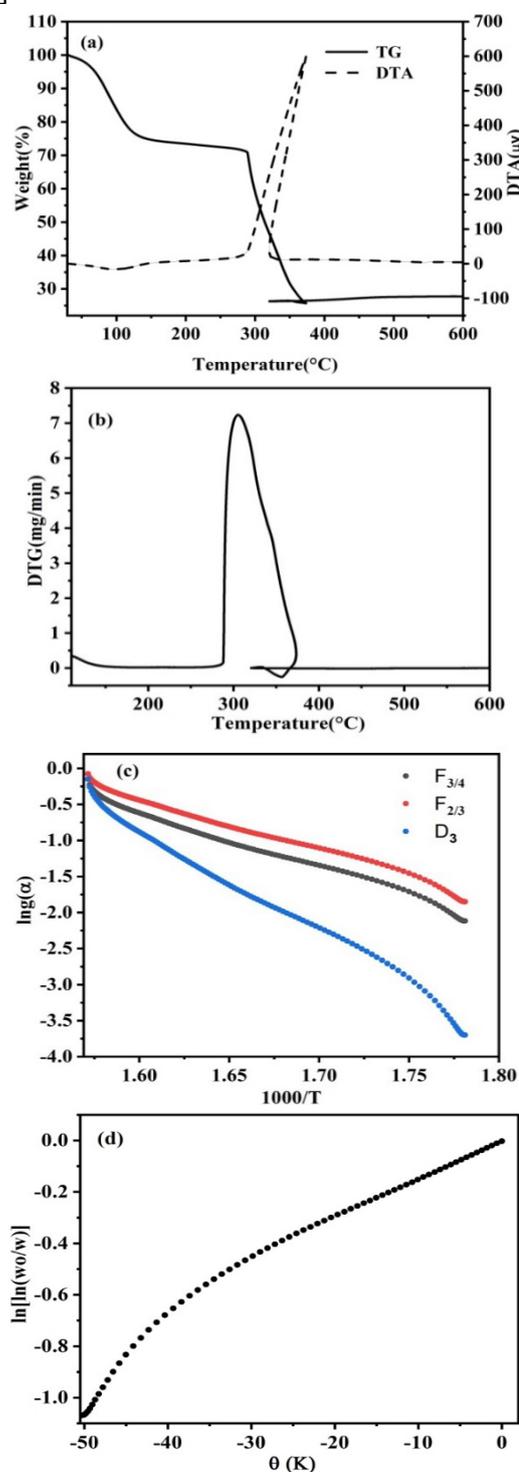


Figure 1. Graph obtained by (a) TG and DTA (b) DTG (c) Coats-Redfern and (d) Horowitz-Metzger method for HKUST-1.

$$\ln \left[\ln \left(\frac{w_0 - w}{w} \right) \right] = \frac{Ea\theta}{RT^2\beta}$$

The slope of $\ln\left[\ln\left(\frac{w_0}{w}\right)\right]$ vs θ is used to determine the activation energy. From the H-M method (Fig. 1d), the value of E_a for single-step decomposition is 67.30 KJ/mol. The best agreement was found with C-R method corresponding to a chemical reaction, i.e., ($F_{3/4}$) documented in Table 3.

Table 2. Activation energy obtained using C-R method for several solid-state processes.

Mechanism	E_a (KJ/mol)	R
P _{1/2}	18.33	0.97585
P _{1/3}	12.22	0.97585
P _{1/4}	9.17	0.97585
P _{3/2}	55.00	0.97585
F _{1/3}	47.66	0.98939
F _{3/4}	67.27	0.99613
F _{3/2}	124.63	0.96240
F ₂	176.71	0.93251
F ₃	298.01	0.90229
F ₀ , P ₁ , R ₁	36.67	0.97585
F _{1/2} , R ₂	54.60	0.99392
F _{2/3} , R ₃	62.72	0.99612
D ₁	73.33	0.97585
D ₂	92.73	0.98729
D ₃	125.44	0.99612
D ₄	102.98	0.99192
A ₁ , F ₁	83.09	0.99105
A _{3/2}	55.39	0.99105
A ₂	41.54	0.99105
A ₃	27.70	0.99105
A ₄	20.77	0.99105

The E_a of decomposition was determined to be 67.29 KJ/mol. This high value reflects the thermal stability of the complex HKUST-1. Thermodynamic parameters ΔG , ΔH are positive whereas ΔS is negative, indicating a non-spontaneous response. The negative value of ΔS implies that the decomposition process occurs at a slower pace than the regular ones. As a result, it is obvious that the thermal decomposition process is unfavorable, signifying that complex HKUST-1 is thermally

stable. Further, to validate our findings, the E_a of Cu complexes with various ligands were compared to the existing results. Cu complexes with 5-(2-carboxyphenylazo)-2-thiohydantoin [35], humic acid [36], pyrazole derivatives [37] and pyridine-dicarboxylate [38] revealed their E_a (KJ/mol) from 74.00 to 136.00, 38.82, 18.70 to 30.20 and 21.40 to 77.50, respectively. In our case, the E_a value of HKUST-1 is found to be 67.29, which is within the range of previously known Cu complexes.

CONCLUSION

The non-isothermal kinetics of HKUST-1 was investigated using simultaneous TG-DTG-DTA. The thermogram of HKUST-1 is of C-type, equivalent to single-step decomposition. The thermodynamic and kinetic parameters were examined using C-R and H-M methods. According to C-R method, thermal degradation of HKUST-1 follows either chemical process or deceleratory path. Further, H-M method, confirms that HKUST-1 follows a chemical process ($F_{3/4}$) in the conversion range considered. The values of A are significantly different using both approaches, whereas the results for the remaining parameters E_a , ΔH , ΔS , and ΔG for $F_{3/4}$ are comparable. As a result, it can be deduced that TG data may be utilised to provide matrices for the decomposition process. The comparison of the findings obtained with different calculating processes revealed that they are highly dependent on the mechanism function of the process selected. Therefore, it is critical to establish the most likely mechanism function for this objective. Some inferences about the mechanisms and features of the processes may be drawn based on accurately determined values of A, E_a , ΔH , ΔS , and ΔG . Hence, different practical concerns requiring solid phase involvement may be addressed.

Acknowledgement: Authors are grateful to Defence Research Development Organization, Ministry of Defence, India, for financial support vide grant No CFEES/TCP/EnSG/CARS/Pantnagar/MOFW/20/20 18 for development of experimental facilities at Pantnagar.

Table 3. Thermodynamic and kinetic parameters of HKUST-1.

Parameters	C-R Method			H-M Method
	F _{3/4}	F _{2/3}	D ₃	
A (min ⁻¹)	4.54 × 10 ⁴	2.10 × 10 ⁴	4.86 × 10 ⁹	5.58 × 10 ¹
E_a (KJ/mol)	67.27	62.72	125.44	67.30
ΔH (KJ/mol)	61.92	57.37	120.08	62.20
ΔS (KJ/mol-K)	-0.16	-0.17	-0.07	-0.26
ΔG (KJ/mol)	166.17	165.73	162.43	219.00

REFERENCES

1. C.J. Wijaya, S. Ismadji, H.W. Aparmarta, S. Gunawan, *Molecules*, **26**(21), 6430 (2021).
2. H.C. Zhou, J.R. Long, O.M. Yaghi, *Chemical reviews*, **112**(2), 673 (2012).
3. T. Shen, T. Liu, H. Mo, Z. Yuan, F. Cui, Y. Jin, X. Chen, *RSC Advances*, **10**(39), 22881 (2020).
4. C.Y. Gao, H.R. Tian, J. Ai, L.J. Li, S. Dang, Y.Q. Lan, Z.M. Sun, *Chemical Communications*, **52** (74), 11147 (2016).
5. H. Jiang, K. Yang, X. Zhao, W. Zhang, Y. Liu, J. Jiang, Y. Cui, *Journal of the American Chemical Society*, **143**(1), 390 (2020).
6. H.Y. Li, S.N. Zhao, S.Q. Zang, J. Li, *Chemical Society Reviews*, **49**(17), 6364 (2020).
7. M.A. Tahir, N. Arshad, M. Akram, *Journal of Energy Storage*, **47**, 103530 (2022).
8. M. Wen, G. Li, H. Liu, J. Chen, T. An, H. Yamashita, *Environmental Science: Nano*, **6**(4), 1006 (2019).
9. B. Yuan, J. Zhang, R. Zhang, H. Shi, N. Wang, J. Li, F. Ma, D. Zhang, *Sensors and Actuators B: Chemical*, **222**, 632 (2016).
10. L. Yang, S. Kinoshita, T. Yamada, S. Kanda, H. Kitagawa, M. Tokunaga, T. Ishimoto, T. Ogura, R. Nagumo, A. Miyamoto, M. Koyama, *Angewandte Chemie International Edition*, **49**(31), 5348 (2010).
11. D. Zhang, J. Zhang, R. Zhang, H. Shi, Y. Guo, X. Guo, S. Li, B. Yuan, *Talanta*, **144**, 1176 (2015).
12. X.J. Liu, Y.H. Zhang, Z. Chang, A.L. Li, D. Tian, Z.Q. Yao, Y.Y. Jia, X.H. Bu, *Inorganic Chemistry*, **55**(15), 7326 (2016).
13. L. Chi, Q. Xu, X. Liang, J. Wang, X. Su, *Small*, **12**(10), 1351(2016).
14. Z. Dong, Y. Sun, J. Chu, X. Zhang, H. Deng, *Journal of the American Chemical Society*, **139**(40), 14209 (2017).
15. X. Wang, P.C. Lan, S. Ma, *ACS Central Science*, **6**(9), 1497 (2020).
16. G. Mouchaham, S. Wang, C. Serre, *Metal-Organic Frameworks: Applications in Separations and Catalysis*, 1 (2018).
17. E. T. Vogt, B. M. Weckhuysen, *Chemical Society Reviews*, **44**(20), 7342 (2015).
18. K.W. Chapman, G.J. Halder, P.J. Chupas, *Journal of the American Chemical Society*, **131**(48), 17546 (2009).
19. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J.F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.S. Chang, *Nature Materials*, **9**(2), 172 (2010).
20. J.S. Shukla, M.G.H. Zaidi, S.K. Dixit, *Asian Journal of Chemistry*, **6**(4), 739 (1994).
21. P. Varshney, S.K. Gururani, R. Singh, M.G.H. Zaidi, *Material Science Research India*, **4**(2), 353 (2007).
22. T. D. Bennett, T. K. Todorova, E. F. Baxter, D. G. Reid, C. Gervais, B. Bueken, B. van de Voorde, D. De Vos, D. A. Keen, C. Mellot-Draznieks, *Physical Chemistry Chemical Physics*, **18**(3), 2192 (2016).
23. R. R. Salunkhe, Y. V. Kaneti, J. Kim, J. H. Kim, Y. Yamauchi, *Accounts of Chemical Research*, **49**(12), 2796 (2016).
24. D. Umeyama, S. Horike, M. Inukai, T. Itakura, S. Kitagawa, *Journal of the American Chemical Society*, **137**(2), 864 (2015).
25. L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud, C. Lamberti, *Chemistry of Materials*, **23**(7), 1700 (2011).
26. R. G. Chaudhary, P. Ali, N. V. Gandhare, J. A. Tanna, H. D. Juneja, *Arabian Journal of Chemistry*, **12**(7), 1070 (2019).
27. V. Rani, R. C. Srivastava, H. M. Agarwal, M.G.H. Zaidi, *Materials Today: Proceedings*, **4**(9), 9471 (2017).
28. K. C. Chong, S. O. Lai, S. K. Mah, H. San Thiam, W. C. Chong, S. H. Shuit, S. S. Lee, W. E. Chong, in: *IOP Conference Series: Earth and Environmental Science*, **1135**(1), 012030 (2023).
29. L. Vlaev, N. Nedelchev, K. Gyurova, M. Zagorcheva, *Journal of Analytical and Applied Pyrolysis*, **81**(2), 253 (2008).
30. L. Núñez, F. Fraga, M.R. Nunez, M. Villanueva, *Polymer*, **41**(12), 4635 (2000).
31. S. Mehtab, M.G.H. Zaidi, N. Rana, K. Khati, S. Sharma, *Bulletin of Materials Science*, **45**(3), 162 (2022).
32. P. Joshi, G. Bisht, S. Mehtab, M.G.H. Zaidi, *Materials Today: Proceedings*, **62**, 6814 (2022).
33. S. Mehtab, M.G.H. Zaidi, N. Rana, K. Khati, S. Sharma, *Bull. Mat. Sci.* **45**, 162(2022).
34. W.W. Lestari, M. Adreane, C. Purnawan, H. Fansuri, N. Widiastuti, S.B. R Ahardjo, in: *IOP Conference Series: Materials Science and Engineering*, **107**(1), 012030 (2016).
35. S. S. Kandil, G. B. El-Hefnawy, E. A. Bakr, A.Z. Abou El-Ezz, *Transition Metal Chemistry*, **28**, 168 (2003).
36. A. G. Prado, J. D. Torres, P. C. Martins, J. Pertusatti, L. B. Bolzon, E. A. Faria, *Journal of Hazardous Materials*, **136**(3), 585 (2006).
37. I.M. El-Deen, A.F. Shoair, M.A. El-Bindary, *Journal of molecular liquids*, **249**, 533 (2018).
38. O.Z. Yeşilel, İ. İlker, M.S. Refat, H. Ishida, *Polyhedron*, **29**(11), 2345 (2010).