Supplementary Information

High-Temperature Oxidation Kinetics of Nanostructured Thermoelectric Skutterudite $CoSb_3$ Under Different Environments

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1. Kinetic computations

For kinetic computation, ICTAC recommendations were followed.[1] For the computation of kinetic parameters a nonlinear integral isoconversional method, Vyazovkin's method [2] was employed. The kinetics of the thermal analysis consider the rate to be a function of only two variables: temperature (T) and extent of conversion (α). This can be expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

The temperature dependence of the rate is given by the Arrhenius equation, Eq (2), and accordingly Eq (1) can be modified to Eq (3)

$$k(T) = A\,exp\left(\frac{-E}{RT}\right) \qquad (2)$$

$$\frac{d\alpha}{dt} = A\,exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (3)$$

Where, k(T) is the rate constant, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant.

The isoconversional method assumes that, at a constant conversion rate, the rate is only a function of temperature. For non-isothermal heating conditions heating rate β is given by,

$$\beta = \frac{dT}{dt}$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\left(\frac{E}{RT}\right)} f(\alpha) \qquad (4)$$

Integration of equation (4)

$$g(\alpha) = \frac{A}{\beta} \int_0^T exp\left(\frac{-E}{RT}\right) dT \qquad (5)$$

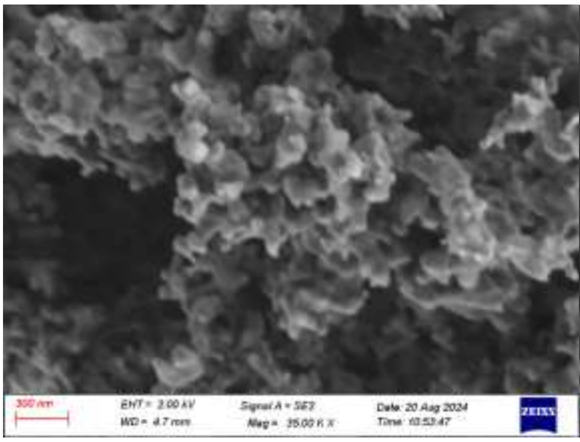
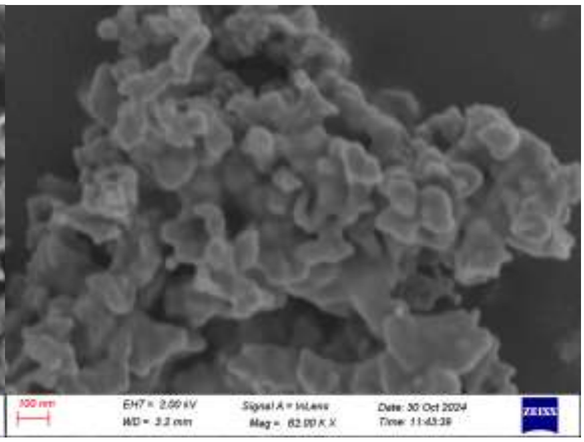
This integration does not have any analytical solution. According to Vyazovkin's method for 'n' runs performed at different heating rates the E_α values can be determined by minimizing the following equation,

$$\phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j\neq 1}^{n} \frac{I(E_\alpha, T_{\alpha,i})\beta_i}{I(E_\alpha, T_{\alpha,j})\beta_j} \qquad (6)$$

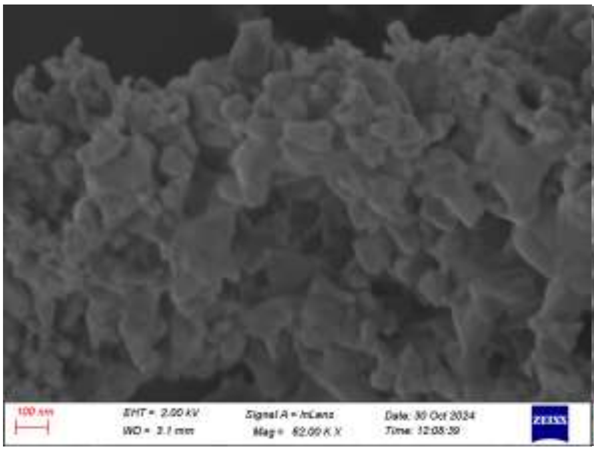
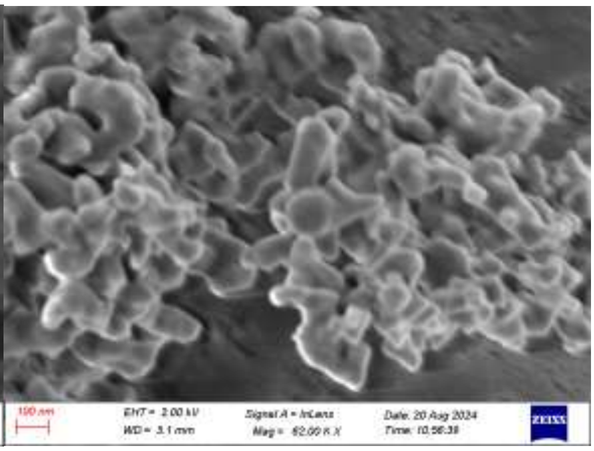
Where the temperature integral (6) is solved numerically, using the third-degree approximation proposed by Senum and Yang[3]

$$I(E_\alpha, T_\alpha) = \int_0^{T_a} exp\left(\frac{-E_\alpha}{RT}\right) dT \qquad (7)$$

2. Characterisation details

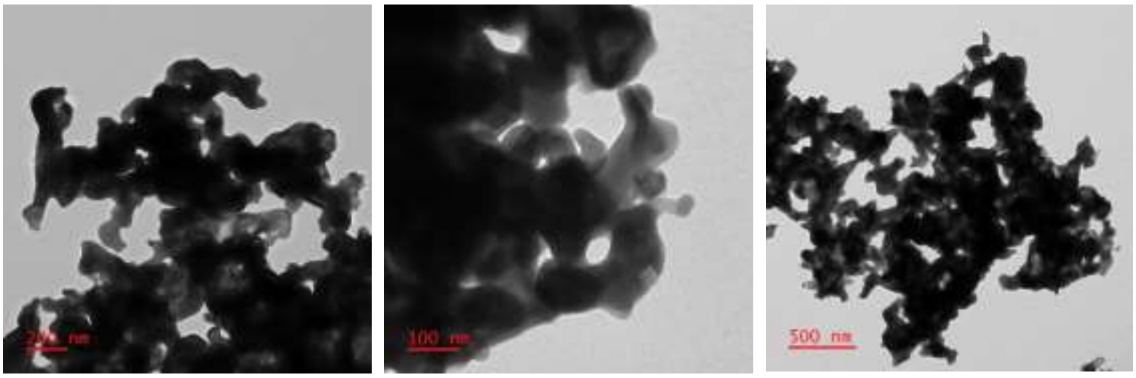



(a) (b)

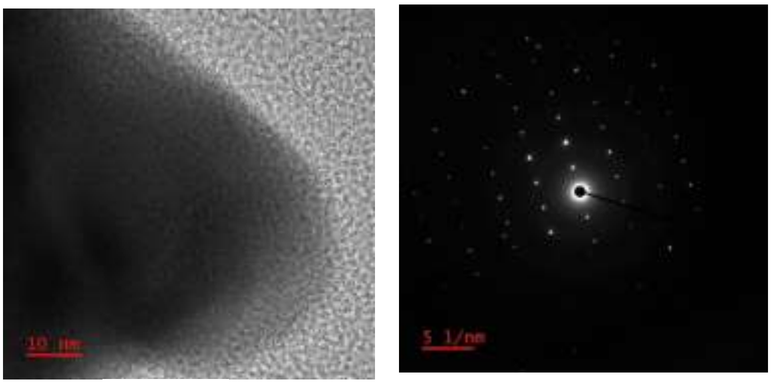



(c) (d)

Fig. S1 SEM images of $CoSb_3$ obtained (a) at optimized reaction conditions (1: 2.8 equivalents of reactants and reaction duration of 72 h) and SEM images showing morphology evolution from cassini oval to plate-like shape over the increment of the reaction duration from (b) 24 h to (c) 48 h and 72 h.

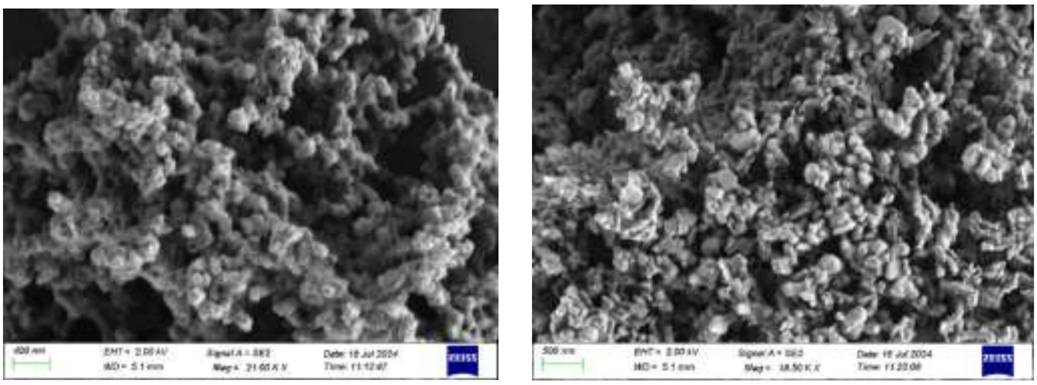


(a) (b) (c)



(d) (e)

Fig. S2 (a-c) TEM images of $CoSb_3$ particles with different morphology (d) HRTEM image and (e) SAED pattern of $CoSb_3$.



(a) (b)

Fig. S3 SEM images of TGA residue from room temperature to 700 °C in (a) air and (b) N_2 atmosphere.

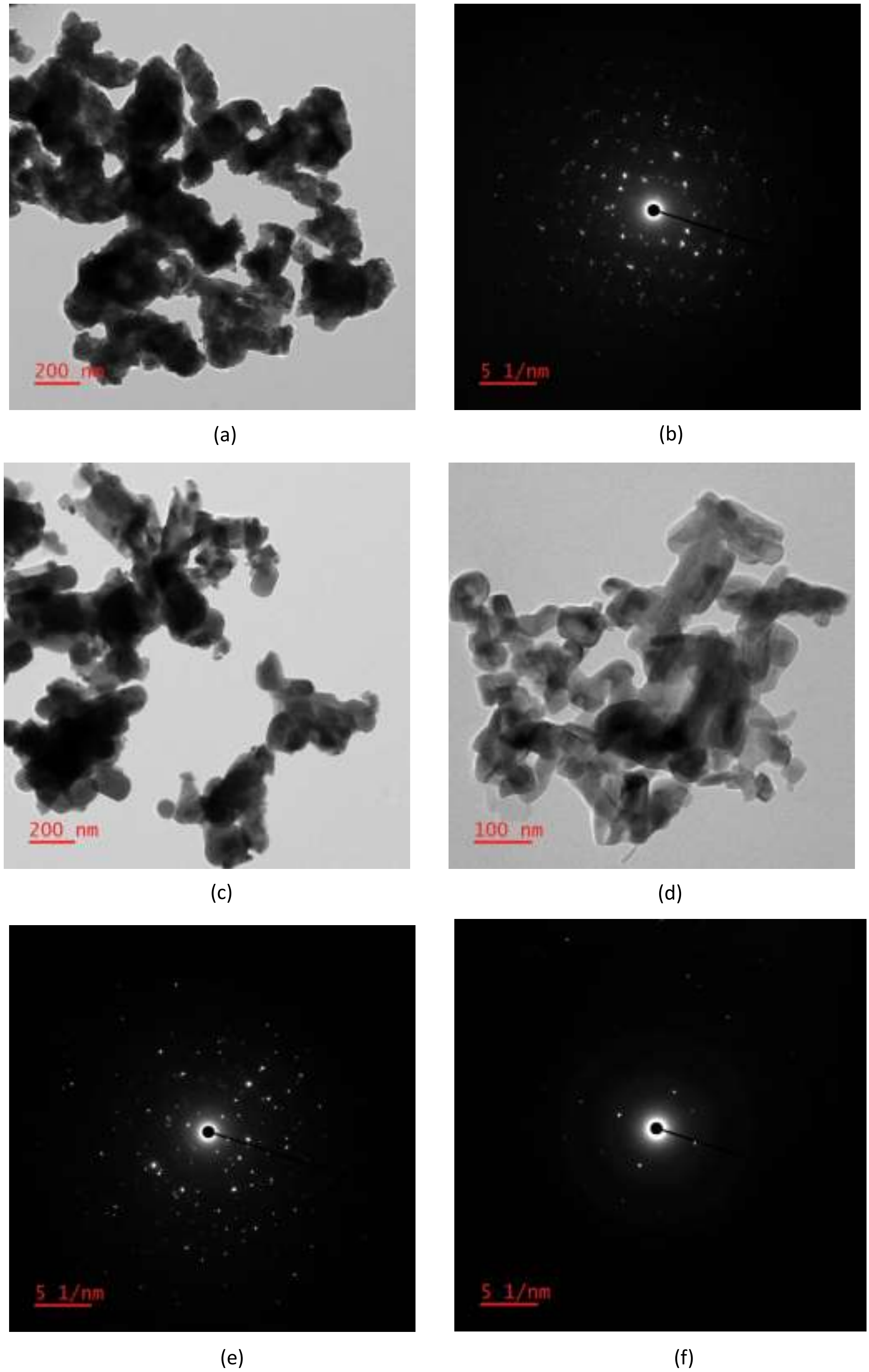


Fig. S4 (a) TEM image and (b) SAED pattern of TGA residue from room temperature to 700 °C in the air (c-d) TEM images of the particles of different morphology and (e-f) SAED pattern of TGA residue from room temperature to 700 °C in N_2 atmosphere.

3. Thermal analysis data

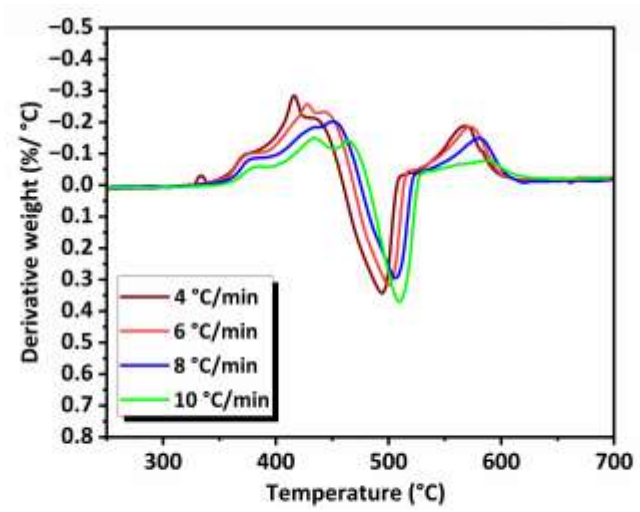


Fig. S5 DTG curves of $CoSb_3$ in air at different heating rates.

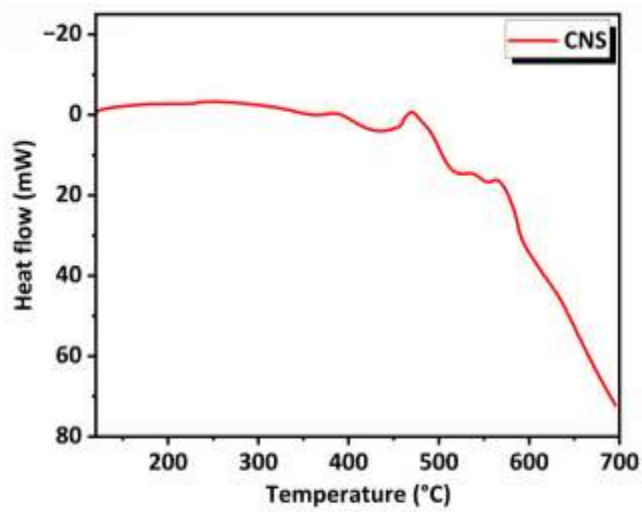


Fig. S6 DTA curve of $CoSb_3$ in N_2 atmosphere. (Performed using Perkin Elmer Simultaneous Thermal Analyser (STA 6000)

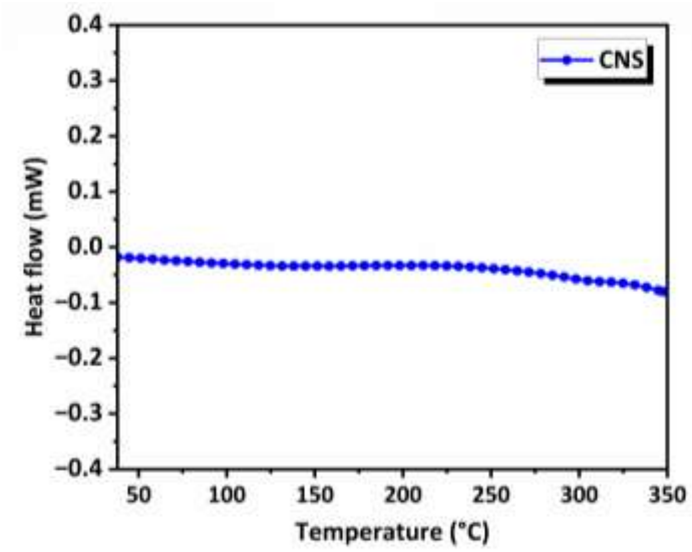


Fig. S6 DSC curve of $CoSb_3$ in N_2 atmosphere.

4. Kinetic analysis data

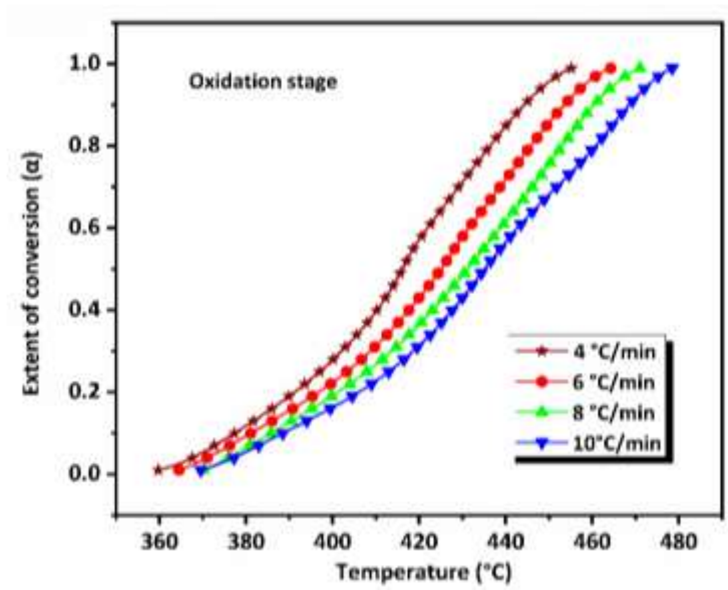


Fig. S7 Extent of conversion vs Temperature curve of oxidation stage.

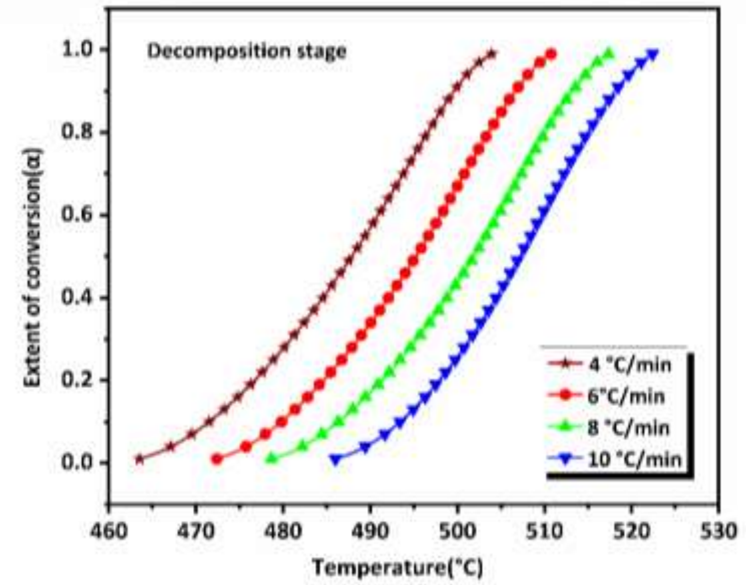


Fig. S8 Extent of conversion vs Temperature curve of decomposition stage.

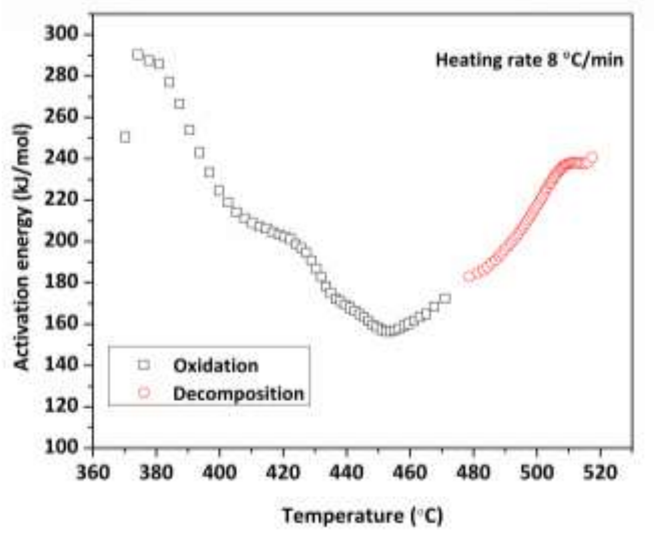


Fig. S9 Combined E_α vs Temperature curve for oxidation and decomposition stages of $CoSb_3$.

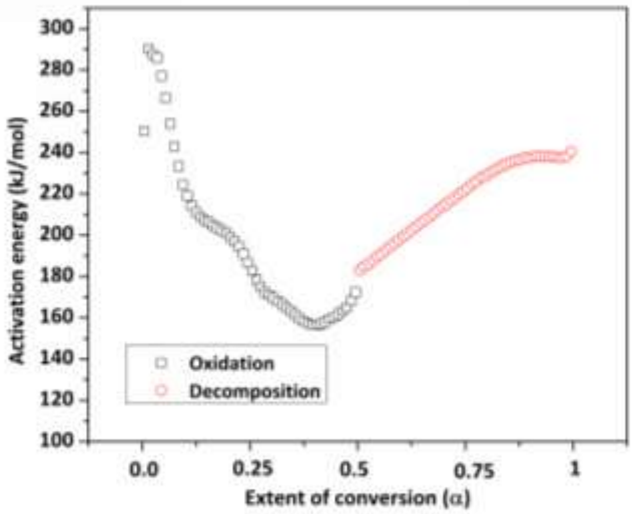


Fig. S10 Combined α vs E_α curve for oxidation and decomposition stages of $CoSb_3$.

5. Degradation products of $CoSb_3$

Sl. No	Compounds	RT-700 °C		Up to maximum weight gain		Up to maximum weight loss	
		Air	N_2	Air	N_2	Air	N_2
1	$CoSb_2O_6$	✓	✓		✓		✓
2	Sb_2O_5	✓	✓	✓	✓	✓	✓
3	Sb_2O_4	✓	✓	✓	✓	✓	✓
4	Co_3O_4		✓	✓	✓	✓	✓
6	$(Co_7Sb_2O_{12})_{2.667}$		✓	✓			✓
7	Sb_2O_3		✓	✓	✓	✓	✓
9	$CoSb_3$			✓			
10	Sb_6O_{13}				✓		
12	CoSb				✓		✓
13	Sb_4O_6						✓

Table. S1 Details of the compounds observed in the PXRD pattern of TGA residues from different stages in air and N_2 atmosphere

References

1 S. Vyazovkin, A. K. Burnham, L. Favergeon, N. Koga, E. Moukhina, L. A. Pérez-Maqueda and N. Sbirrazzuoli, *Elsevier B.V.*, 2020, preprint, DOI: 10.1016/j.tca.2020.178597.

2 S. Vyazovkin and D. Dollimore, *Linear and Nonlinear Procedures in Isoconversional Computations of the Activation Energy of Nonisothermal Reactions in Solids*, 1996.

3 G. I. Senum and R. T. Yang, *J. Thermal Anal*, 1977, **11**, 445–447.