



Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) of some synthesized metal nanoparticles

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Abstract: Nanoparticles reveal exceptionally interesting thermal properties which make them an impending material for use in various heat transfer devices. Current paper deal with Nanoparticles of Al, Na, CdTe and Fe has been synthesized. Thermal activity of nano materials is exciting for understanding of composition as well as impurities. TGA (Thermogravimetric analysis) reveals to carry out thermodynamic parameters of all metal samples. Kinetic parameters, such as thermal activation energy, enthalpy, entropy & gibbs energy, have been calculated from Thermograms. The thermal stability of these nano particles was investigated using Differential scanning calorimetry (DSC) on the basis of heat-absorbing. The Differential scanning calorimetry (DSC) with all the empirical evidence mentioned briefly in the current study. The activation energy and all thermodynamic parameters for all phases of decomposition have been determined using the Coats-Redfern process. The outcome and appearance of thermal parameter were discussed in the related sections.

Keywords: Coats-Redfern Method, Decomposition, Thermogravimetric Analysis, Differential Scanning Calorimetry, Diffusion Control.

1. INTRODUCTION :

Aluminum particles are extensively used in propulsion and energy-conversion applications due to their high oxidation enthalpy, relative safety, and low cost [1]. When a nascent aluminum particle is exposed to an oxidizing environment at room temperature, the chemical reactions between the aluminum atoms and oxidizer molecules result in the formation of an amorphous aluminum oxide (Al_2O_3) layer on the particle surface [2]. Typically, the rate of heat-release due to these chemical reactions is lower than that of heat loss to the surrounding environment. As a result, the particle does not ignite and the thickness of the oxide layer saturates at a value in the range of 0.5–4 nm, depending on the temperature and duration of exposure to the oxidizing gas [2]. The oxide layer protects the aluminum core from further attack of the oxidizer molecules. The ignition temperature of passivated aluminum particles decreases from 2350 K (melting point of the oxide layer) at 37°C to 1000°C (melting point of the aluminum core) at 660°C [3]. The enhanced reactivity of nano-sized particles poses significant safety hazards. If the size of the particle is decreased below a critical value, the particle could ignite when exposed to an oxidizing gas at room temperature, a phenomenon known as pyrophoricity [4]. It is a major safety issue during particle manufacture, handling, and storage. It can also be employed for useful applications like decoy flare for defending heat-seeking missiles [5]. Reliable measurements or predictions of the critical particle size for pyrophoricity are of paramount interest.

For metal nano particles experimental study of oxidation, thermogravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) is the preferred method to give valuable information on the activation energy [4] and reactivity of the powders. The change of crystalline structure during the oxidation is tracked with (transmission electron microscopy (TEM)) and (X-ray powder diffraction (XRD) [5]. Theoretical models for nanopowder oxidation focus on the evolution of the oxide thickness with time and/or temperature, whereas TGA results provide a mass evolution. It is therefore important to determine the oxide thickness from TGA analysis. Different models exist in the possible (1/10 ppm) to ensure that the particles do not come into contact with oxygen during the setup phase of the analysis. A temperature calibration of the thermo-balance was conducted using the melting point standard (DIN 51007) of various metals. The Al and Na nano particles was uniformly placed in an Al_2O_3 crucible of 6.8 mm diameter and 85 l volume. The powder was forming a uniform layer in the crucible.

2. EXPERIMENTAL PROCEDURE :

Nanoparticles of CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) samples are pre- pared using a chemical co-precipitation process. Each chemical nano particles are of analytical reagent grade and are used lacking advance purifi- cation. Recently formulated aqueous solutions of chemicals are used for nanoparticles severance.

Metal nanoparticles CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) are prepared by plummeting concur- rently 60 ml of 0.4 M solution of Metal nanoparticles CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver), into 60 ml of 0.0125 M solution of ethylene diamine tetraacetic acid which is dynamically stirred using a magnetic-stirrer. The task of EDTA used was to balance the particles adjacent to aggregation which may escort to nano size of the particle. The metal-carbonate impulsive created out of this reaction which is alienated from the reaction mixture and is washed many times with purified water and again through alcohol to take away contaminations, including waste of (EDTA) as well as also removes original reactant if any present. The wet precipitate is dehy- drated and systematically ground using an agate-mortar to acquire metal-carbonate antecedent in the form of very fine powder. On high required temperature the metal-carbonate antecedent (con-vert) into CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) nanoparticles.

Thermogravimetric analysis of the CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) nanoparticles analysed by thermo-gravimetric analyzer (METTLER TOLEDO TGA-1) from 27 °C to 990 °C with an argon flow-rate of 20ccpm and a heating-rate of 10 °C/min. Thermal degradation of all the CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) nanoparticles loadings was calculated by thermogravi- metric analysis with actions alike to those used for the nanoparticles. The activation-energy (E_a) and some other thermal parameter for CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) were obtained by the Coats and Redfern method.

3. RESULTS AND DISCUSSION :

The Thermal analysis for CdTe (Cadmium telluride), Fe (Iron), Na (Sodium), and Ag (Silver) nanoparticles using the TGA and DSC analysis techniques plays an important role in investigating the behaviour of composites and polymers under a constant gradual increase in temperature. Conversely, this thermal process is affected by environmental and compound properties respectively temperature increasing. TGA and DSC analysis looked at pure epoxy and a blend at different weight percentages of CdTe, Fe, Na and Ag nanoparticles. This thermal experiment were performed at a temperature range of 25°C to 1000°C by employing a constant heating rate of 10°C/min except for the pure epoxy, for which the heating rates were 5°C/min and 10°C/min.

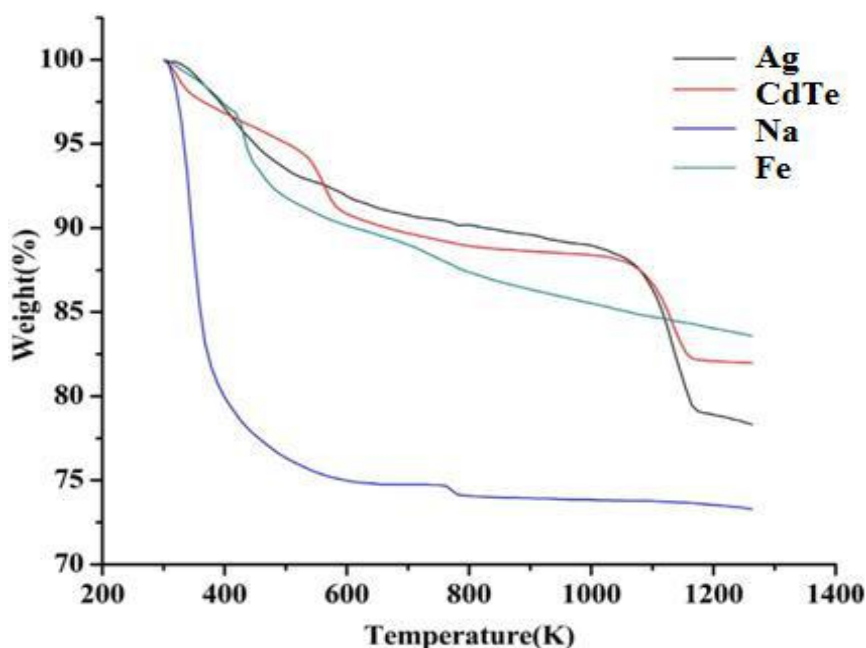


Figure.1: Thermogram for Ag, CdTe, Fe and Na Nanoparticles



The thermogram for Ag, CdTe, Fe and Na Nanoparticles reveals by TGA showed weight loss in one and two steps. The first degradation loss due to removal of moisture and other volatiles as well as elimination of pendant groups such that followed by random backbone chain scission. The thermal depolymerisation which is took place at the end of the chain until a monomer is gradually achieved for nano material. The DSC analysis show curves very clearly the glass transition of epoxy. Its nano composites followed by two exothermic peaks which represent the entire decomposition. DSC curves (Figure-1) shows that epoxy at a heating rate of 5°C/min decompose in two stages. As par result the first stage of decomposition occurs between 114°C and 417.6°C with a mass loss of 94.67%, while the second occurs at 417.6°C to 645.7°C with a mass loss of 19.56%. From the DSC analysis it can be seen that the glass transition temperature is 71°C followed by two exothermic peaks: the first represents volatile removal which occurs at 378.4°C with a heat flow of 3.0 μV, and the second occurs at 504.8°C with a heat flow of 43 μV, which is considered much higher compared to the volatile removal step shows in table 1.

Table-1: Thermogravimetric analyses of metal nanoparticles.

Nanoparticle Mass loss (%) at different temperature

	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K	1100 K	1200 K	1263 K
Ag	0	2.77	6.63	8.2	9.26	9.83	10.4	11.05	13.6	21.14	21.67
CdTe	0	1.04	4.87	9.22	10.34	11.07	11.38	11.6	13.54	17.93	18.02
Na	0	19.94	23.27	25.05	25.26	25.93	26.07	26.16	26.23	26.47	26.72
Fe	0	2.6	8.08	9.91	11.03	12.64	13.65	14.47	15.25	15.95	16.43

4. KINETICS ANALYSIS FOR METAL NANOPARTICALS :

According to the DSC analysis that the Different reaction models have been employed to determine the kinetic data of thermal decomposition; however, the results vary widely as shown in Table 1. The current study, the diffusion-controlled model was built-in to the practical data with an R2 correlation equal to 100% of thermal decomposition epoxy at 5°C/min. The thermal reaction which is take place at the outer surface with a thin layer gradually such that traveling towards the interior of the particles. This phenomenon occurs when the porosity is very small [11]; in other words that the reaction takes place very quickly at the outer surface and the diffusion magnitude is very small.

The Coats–Redfern model is a multi-heating rate [12], [13] used in determining the activation energy and frequency factor through diffusion control (Janders):

$$\ln \left[\frac{g(x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \right] \left[1 - \left(\frac{2RT}{E} \right) \right] - \left(\frac{E}{RT} \right)$$

$$g(x) = [1 - (1 - \alpha)^{1/3}]^2$$

where (1-α) is fractional remaining of sample, β is heating rate, A is frequency factor, R is gas constant, T is decomposition temperature and E is activation energy.

Plotting g(x) against 1/T for each heating rate produce a straight lines of slope of (-E/R). Frequency factor directly determined from intercept at Y axis:

$$Intercept = \ln \left[\frac{AR}{\beta E} \right] \left[1 - \frac{2RT}{E} \right]$$



Figures 8 and 9 show a plot of Coats-Redfern $g(x)$ against $1/T$ which gives a linear relationship with a high correlation R^2 close to 100% and this confirms that the chosen model is correct.

For both Coats and Redfern and Horowitz-Metzger methods, the correlation coefficient values among the reaction of different orders are considered (Ebrahimi-Kahrizsangi, .2008) [21]. The value of (y) is referring to different region of degradation as determined at different temperature interval from TG curve. According to Coats and Redfern and Horowitz-Metzger methods [20].

A plot of $\ln [-\ln g(y) / T^2]$ versus $1000/T$ for major degradation events yielded straight line and slope. This slope is equal to $-E_a / 2.303 R$ and intercept of $\ln AR / \beta E_a [1 - (2RT/E)]$.

The value of activation energy (E) and pre-exponential factor (A) was calculated from the slope and intercept of the best linear fit curve respectively. Through below equation evaluate to some other kinetic parameter such as entropy of activation, enthalpy of activation, Gibbs energy of activation is express by

$$\text{Entropy} \quad S^* = 2.303 \cdot R \cdot \log \left(\frac{Ah}{kT} \right)$$

$$\text{Enthalpy} \quad H^* = E^* - RT$$

$$\text{Gibbs energy} \quad G^* = H - TS$$

Where,

- h is Planck's constant ($6.626 \times 10^{-34} \text{ j} \cdot \text{s}$)
- k is Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$)

The value of E_a , S^* and G^* for CdTe, Fe, Na, and Ag nanoparticles are presented in Table 2.

Table.2: Kinetic Parameter for Ag, CdTe, Na and Fe Nanoparticles.

Nanoparticle	Stage	Temp range (K)	Ea(kJ/mol)	DH(kJ/mol)	DS(J/K)	DG(J/K.mol)
Ag	I	319–418	—86.8593	—6763	—42.3106	28041.73
	II	427–1067	—15.2877	—6691.43	—42.2027	27970.27
	III	1076–1263	—285.77	—6961.91	—42.6106	28240.34
	IV	319–1263	—33.546	—6709.7	—42.23	27988.5
CdTe	I	339–555	—21.7109	—6697.85	—42.2123	27976.68
	II	575–1057	—11.0096	—6687.15	—42.1962	27,966
	III	1067–1263	—282.995	—6959.14	—42.6064	28237.57
	IV	339–1263	—28.625	—6704.8	—42.223	27983.6
Na	I	309–368	—163.574	—6839.72	—42.4263	28118.33
	II	378–1116	—12.3352	—6688.48	—42.1982	27967.32
	III	1126–1263	—74.6191	—6750.76	—42.2921	28029.51
	IV	309–1263	—22.44	—6698.6	—42.213	27977.4
Fe	I	319–427	—56.724	—6732.87	—42.2652	28011.64
	II	447–1067	—22.2827	—6698.42	—42.2132	27977.25
	III	1076–1263	—93.0455	—6769.19	—42.3199	28047.91
	IV	309–1263	—33.573	—6709.7	—32.11	21288.9

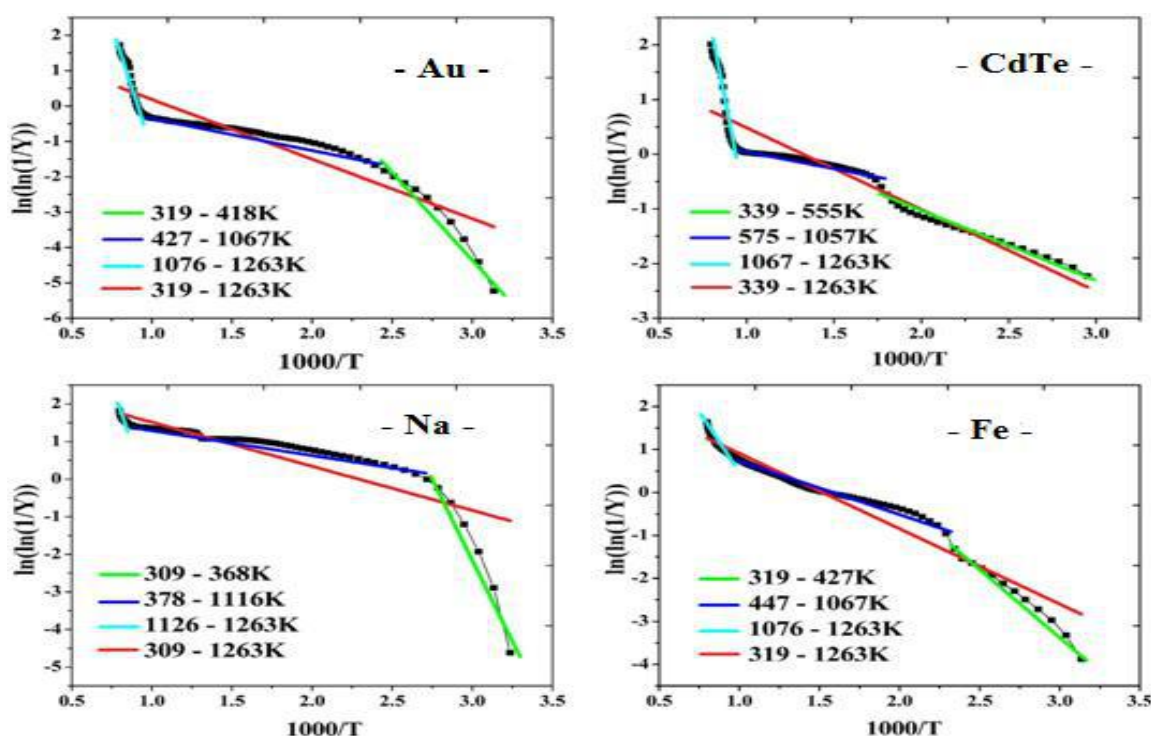


Figure.2: Plot of $\ln(\ln(1/Y))$ Vs $1000/T$ for metal nanoparticles.

According to experimental results of kinetics data and thermodynamic properties for Metal nanoparticles CdTe, Fe, Na, and Ag are shown in Table 2. The results seen the nanoparticles activation energy increases with increasing the weight percentage of CdTe (Cadmium telluride) and Fe (Iron) since the latter contribute in stiffness and rigidity of polymer chains and this will increase the thermal stability of composite under elevated temperature. The percentage of CdTe (Cadmium telluride) and Fe (Iron) has a significant effect on reaction rate constant and entropy, which increases with increasing CdTe (Cadmium telluride) and Fe (Iron) content at a higher decomposition temperature due to increased rates of collisions. Activation energy also increases because of the increased thermal stability and reduction in early decomposition periods; however, there is more bonding, which means more heat is required to break it. The total enthalpy of decomposition of the two stages increases with increasing CdTe (Cadmium telluride) and Fe (Iron) content, as these particles retain the heat evolved; therefore, the process takes a short time to dissipate heat because it resists heat transfer due to its low thermal conductivity [21], [22].

The relationship between logarithm magnitude of frequency factor and activation energy is always linear, meaning at a higher temperature, the activation energy and rate constant will be higher due to an increase in the collision rate amongst the molecules, suggesting the reaction model should be selected carefully, as shown in Figure 2.

The activation energies of decomposition were negative for all four CdTe, Fe, Na and Ag metal nano-particles; it means that the rate of reaction decreases as temperature increases. The higher values of the energy of activation tells that the thermal immovability of the CdTe, Fe, Na and Ag metal nano-particles. The entropy and enthalpies of activation [DS & DH] values for different parts of four CdTe, Fe, Na and Ag metal nano-particles are negative which are compensated by the each other's values leading to approximately the identical values (21288–28118 kJ mol⁻¹) for the gibbs free energies of activation [DG]. The statistics were recapitulated in Table 2. The entropy of activation [DS] had negative-values in CdTe, Fe, Na and Ag nano-particles, which specifies that the reactions of decomposition carry on with a lower speed than usual ones.

5. CONCLUSION :

The thermal study reveals the mass degradation of all four metal nano-particles in one or two steps at a certain temperature which is indicated in the results. The relative weight loss measured at an increase in temperature at a speed of 10°C/minute using TGA also. Na nanoparticle was instant degradation at around 400 to 800 K and nanoparticles of CdTe, Fe and Ag were degraded at high temperatures at around 800 to 1000 K. DSC analysis reveals the Negative



activation energy revealed a decreased reaction rate with increased temperature and negative values of activation entropy and activation enthalpy, as well as a positive value of Gibbs free energy which shows no freezing for all CdTe, Fe, Na and Ag nano particles. This kinetic parameter explicitly indicates that degradation is not random.

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