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Research Article

Sublimation Kinetic Studies of the $Zr(tmhd)_4$ Complex

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The thermal behaviour of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium(IV), $[Zr(tmhd)_4]$ was investigated by nonisothermal and isothermal thermogravimetric methods in a high pure nitrogen atmosphere. The influence of the heating rate in dynamic measurements (6, 8, 10, and 12°C/min) on activation energy was also studied. The nonisothermal sublimation activation energy values determined following the procedures of Arrhenius, Coats and Redfern, Kissinger, and Flynn-Wall yielded 76 ± 5, 92 ± 2, 81 ± 8, and 72 ± 7 kJ/mol, respectively, and the isothermal sublimation activation energy was found to be 87 ± 4 kJ/mol over the temperature range of 411–462 K. Different reaction mechanisms were used to compare with this value. Analysis of the experimental results suggested that the actual reaction mechanism was an R_n deceleration type.

1. Introduction

Metal β-diketonates are promising materials for obtaining high-purity and fine-particle metal oxides with potential high-temperature applications [1]. Zirconium dioxide (ZrO_2) has low electrical conductivity, is chemically inert, has relatively low dielectric constant [2], and has wide energy band gap, high index of refraction, and good mechanical and chemical stability. The use of dielectric films in microelectronic devices as well as sensors [3], antireflective coatings, and mirrors [4] have attracted considerable interest in ZrO_2. Thin films of ZrO_2 can be used as protective coatings [5], in tunnel junctions [6], gas sensors [7, 8] and in fuel cells [6]. ZrO_2 has also been employed as a barrier layer between a silicon substrate and high-temperature superconducting films [9] and as buffer layers for super conductors and thermal barrier coatings [10]. The high ionic conductivity of stabilized cubic zirconia are ideally suited in applications such as oxygen sensors and fuel cells. Thermal barrier coatings are the components of current and future energy systems and are applied in new generation of high by pass aero engines and gas turbines for power engines to increase the gas inlet temperature [11]. The β-diketonate complexes of zirconium, (tmhd=(2,2,6,6-dimethyl-3,5-heptanedionate) $[Zr(tmhd)_4]$, have high thermal stability which allows the optimized growth of ZrO_2 at a substrate temperature greater than 600°C. Metal β-diketonates $Zr(tmhd)_4$ can be used to deposit pure ZrO_2, and it is thermally stable. This complex sublimes at a relatively low temperature (~400 K) giving high vapour pressure. Herein we report the sublimation kinetics of $Zr(tmhd)_4$ under nonisothermal and isothermal conditions by using Arrhenius, Coats-Redfern, Kissinger, and Flynn-Wall methods.

2. Experimental

Synthesis. The complex $Zr(tmhd)_4$ was synthesized by modifying the procedure of Sievers et al. [12]. Zirconium tetrachloride dissolved in warm aqueous ethanol was mixed with tmhd ligand in a 1 : 4 ratio with constant stirring. The complex formed was filtered, dried, and recrystallized in ethanol.

2.1. Nonisothermal TG. The thermogram of the complex was carried out with Perkin-Elmer Pyris-Diamond TG-DTA. The thermogravimetric analysis was performed at various linear heating rates. Temperature calibration was done by the

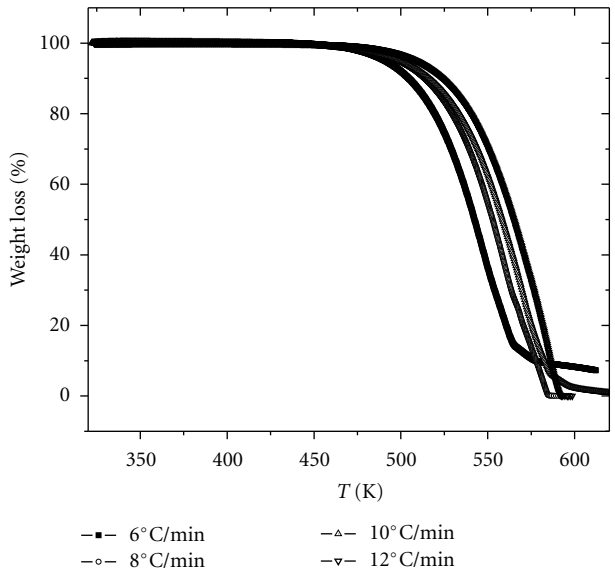

Figure 1: Nonisothermal TG curve of $Zr(tmhd)_4$ at different heating rates.

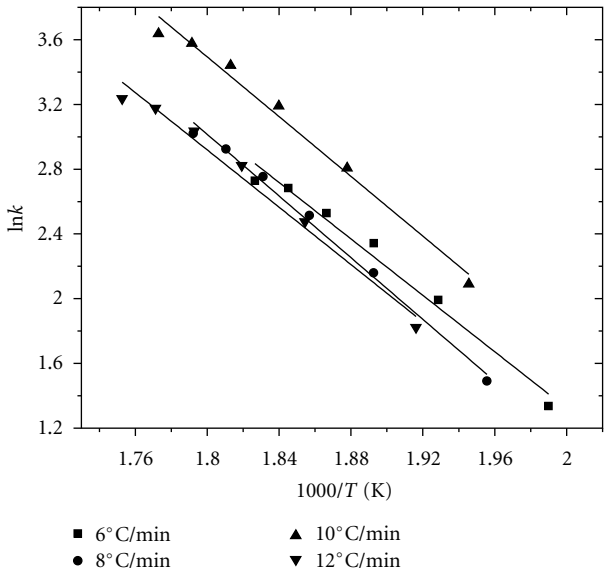

Figure 2: Arrhenius plots of $Zr(tmhd)_4$ at various heating rates.

method of fixed melting points by using International Practical Temperature Scale 1968 (IPTS-68; amended in 1975) recommended standards for indium, tin, and aluminium [13, 14]. Approximately 3 mg of $Zr(tmhd)_4$ was taken for each experiment. Sintered high-density alumina crucibles were used as sample and reference holders, and α-alumina powder was used as the reference material. The purge gas was high-purity nitrogen dried by passing through refrigerated molecular sieves (Linde 4A) at a flow rate of 12 dm^3/h.

2.2. Kinetic Analysis. The conventional nonisothermal thermogravimetric runs were carried out at various heating rates such as 6, 8, 10, and 12°C/min. Also, isothermally programmed thermogravimetric analysis was carried out over the temperature range of 411–462 K in nitrogen atmosphere at the flow rate of 6 dm^3/h. Among the several methods available for the kinetics evaluation of TG weight loss data, Arrhenius, Redfern, and Coats, Kissinger, and Flynn-Wall methods were followed in the present paper to study the sublimation kinetics. From the study of isothermal sublimation kinetics, the activation energy was calculated from the slope of the plot of maximum mass loss rate $[\ln (d\alpha/dt)_m]$ against the reciprocal of several isothermal temperatures (1000/T (K)).

3. Results and Discussions

3.1. Thermal Properties of Zr(tmhd)$_4$. TG-DTA curves of $Zr(tmhd)_4$ (Figure 1) revealed that the weight loss occurred in a single step commencing from 473 K due to solid sublimation showing a nil residue at 628 K. This single-stage weight loss after 473 K provided a wide range of temperature window for the estimation of sublimation enthalpy.

The complete volatility of this complex makes it suitable as the precursor for the MOCVD of ZrO_2.

3.2. Determination of Energy of Activation (E_a)

3.2.1. Nonisothermal Sublimation Kinetics. The rate constant k, for the sublimation of the complex was determined in the 470–550 K range for every 10% weight loss of the complex at different heating rates. The expression for k is given by

$$k = \frac{d\alpha}{dt}, \tag{1}$$

where $d\alpha/dt$ is the derivative of the fraction sublimed with respect to time, and k is the rate constant of sublimation. By using this equation, k was calculated for every 10% weight loss. α is defined by the expression as

$$\alpha = \frac{\%W_i - \%W_t}{\%W_i - \%W_f}, \tag{2}$$

where $\%W_t$ is the percent weight at any time t and $\%W_i$ and $\%W_f$ respectively, are the initial and final percent sample weights [15]. The Arrhenius expression is

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3}$$

and the plot of $\ln k$ versus 1000/T (K) (Figure 2) is linear. From the slope, the activation energy (E_a) for the sublimation of the complex was calculated. The activation energy values obtained are 73±5, 79±3, 77±5, and 74±5 kJ/mol, respectively at the heating rates of 6, 8, 10, and 12°C/min.

The activation energy for the nonisothermal sublimation of $Zr(tmhd)_4$ was calculated using the Kissinger expression:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \left(\frac{n(1-\alpha_m)^{n-1}AR}{E_a}\right) - \left(\frac{E_a}{RT_m}\right), \tag{4}$$

Table 1: Non-isothermal sublimation kinetics of the $Zr(tmhd)_4$ complex.

Heating rate	Arrhenius	Redfern and Coats (R_2)	Kissinger	Flynn-Wall	
(β) (°C/min)	E_a (kJ/mol)		E_a (kJ/mol)	Conversion (α)	E_a (kJ/mol)
6	73 ± 5	88 ± 4	81 ± 8	10	71 ± 7
8	79 ± 3	93 ± 2		20	69 ± 9
10	77 ± 5	90 ± 1		30	72 ± 5
12	74 ± 5	96 ± 1		40	71 ± 8
				50	74 ± 6
				60	76 ± 5
				70	71 ± 6
				80	75 ± 8
E_a (kJ/mol)	76 ± 5	92 ± 2	81 ± 8		72 ± 7

Table 2: Isothermal sublimation kinetics of the $Zr(tmhd)_4$ complex.

Isothermal maximum mass loss rate	
T (K)	$(d\alpha/dt)_m$
411	0.00575
422	0.01172
432	0.02437
442	0.04021
452	0.06326
462	0.09437
E_a (kJ/mol)	87 ± 4

where T_m and α_m are the absolute temperature and weight loss at the maximum weight loss rate $(d\alpha/dt)_m$. This method yielded a value of 81 ± 8 kJ/mol from the slope of $\ln(\beta/T^2_{\max})$ versus $1000/T_{\max}$ (K) at the maximum weight-loss rate (Figure 3).

The activation energy was determined by the Flynn-Wall technique using the expression $\ln\beta = \ln(AE_a/R) - \ln[F(\alpha)] - E_a/RT$ and from a linear fitting of $\ln\beta$ versus $1000/T$ (K) at different conversions. The results of the Flynn-Wall analysis are given in Figure 4, which shows the best fitting straight lines are nearly parallel, indicating the constant activation energy in the range of conversion analysed and confirming the validity of the approach used. Activation energies corresponding to the different models are listed in Table 1. From these values a mean value of 72 ± 7 kJ/mol was found for the weight loss range of 10–80% and this value was found to be comparable with the result of the Arrhenius method (Table 1). Both methods do not require *apriori* knowledge of the reaction mechanism for the determination of activation energy [16].

3.2.2. Isothermal Kinetics. The calculation of activation energy of the isothermal sublimation process was carried out in the temperature range of 411–462 K. The observed mass loss and isothermal temperature are listed in Table 2. The plot of $[\ln(d\alpha/dt)_m]$ against $1000/T$ (K) is shown in Figure 5. The activation energy was found to be 87 ± 4 kJ/mol which was comparable with the enthalpy of sublimation value of 85 ± 4 kJ/mol.

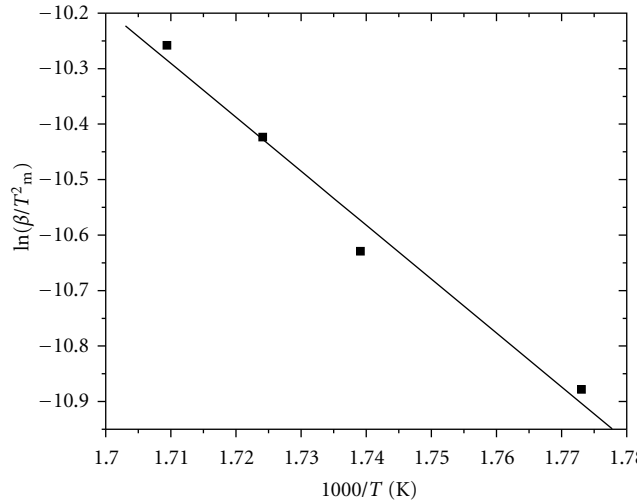

Figure 3: Kissinger plot of $\ln(\beta/T^2{}_m)$ versus $1000/T$ (K).

The activation energy corresponding to different $g(\alpha)$ for sigmoidal and decelerated mechanisms [17] can be obtained at a constant heating rate using the Coats-Redfern equation from a fitting of $\ln[g(\alpha)/T^2]$ versus $1000/T$ (K) plots (Figure 6). Table 3 shows the activation energies and correlations for conversion at constant heating rate values of 6, 8, 10, and 12°C/min. The activation energies are in best agreement with that obtained using the Friedmann's method corresponding to an R_n type mechanism. It can be found from these tables that the better agreement is at the heating rate of 10°C/min, at which the activation energy corresponding to R_2 (90 kJ/mol) agrees with the value of 87 kJ/mol obtained from the Arrhenius method. These facts suggest [17] that the solid-state reaction mechanism for the sublimation of $Zr(tmhd)_4$ is a deceleration (R_2) type.

4. Conclusion

The nonisothermal sublimation activation energy values determined following the procedures of Arrhenius, Coats and Redfern, Kissinger, and Flynn-Wall yielded 76 ± 5, 92 ± 2, 81 ± 8, and 72 ± 7 kJ/mol, respectively. The activation

Table 3: Activation energies obtained using the Redfern-Coats method for several solid state processes at the heating rates of 6, 8, 10, and 12°C/min for $Zr(tmhd)_4$.

Mechanism	6°C/min		8°C/min		10°C/min		12°C/min	
	E_a (kJ/mol)	R	E_a (kJ/mol)	R	E_a (kJ/mol)	R	E_a (kJ/mol)	R
A2	50 (±0.7)	0.9991	50 (±0.9)	0.9989	49 (±2)	0.9963	52 (±2)	0.9957
A3	30 (±0.5)	0.9989	31 (±1)	0.9887	30 (±1)	0.9956	31 (±1)	0.9950
A4	21 (±0.4)	0.9987	21 (±0.4)	0.9986	20 (±0.7)	0.9950	21 (±1)	0.9940
R2	88 (±4)	0.9929	93 (±2)	0.9988	90 (±1)	0.9997	96 (±1)	0.9999
R3	94 (±3)	0.9963	98 (±1)	0.9996	95 (±1)	0.9994	101 (±1)	0.9994
D1	152 (±12)	0.9791	166 (±7)	0.9935	162 (±5)	0.9969	173 (±4)	0.9977
D2	171 (±10)	0.9884	183 (±5)	0.9974	178 (±3)	0.9992	190 (±2)	0.9996
D3	197 (±6)	0.9968	204 (±2)	0.9996	200 (±3)	0.9995	212 (±3)	0.9994
D4	179 (±9)	0.9920	190 (±4)	0.9985	185 (±2)	0.9997	197 (±1)	0.9999
F1	109 (±2)	0.9992	109 (±2)	0.9990	107 (±3)	0.9968	113 (±4)	0.9963
F2	88 (±19)	0.8701	65 (±14)	0.8697	63 (±15)	0.8481	65 (±16)	0.8445

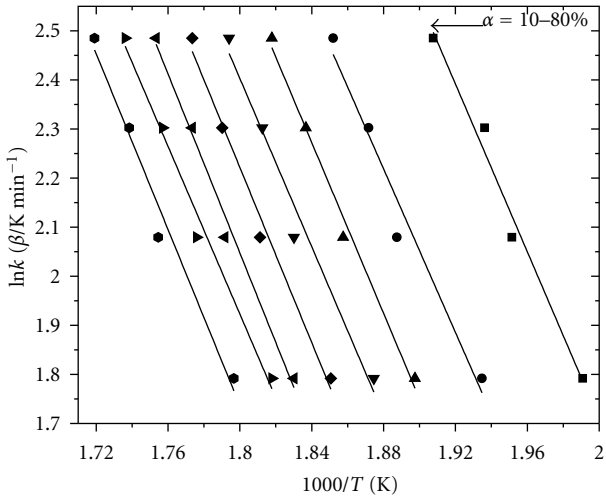

Figure 4: Flynn-Wall plots of $Zr(tmhd)_4$ at different heating rates.

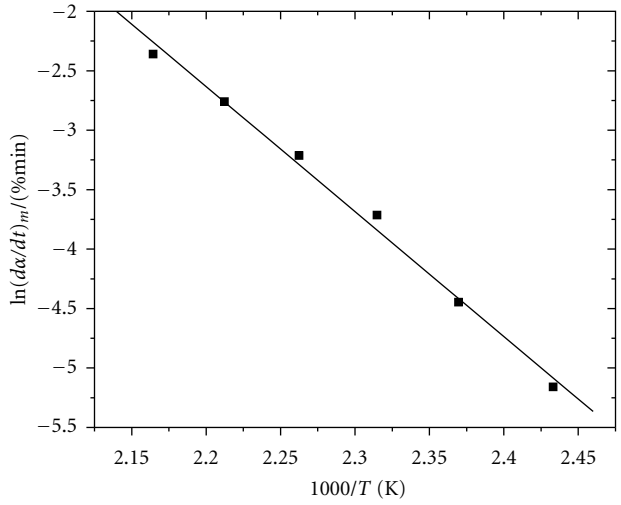

Figure 5: Friedmann isothermal plot of $Zr(tmhd)_4$.

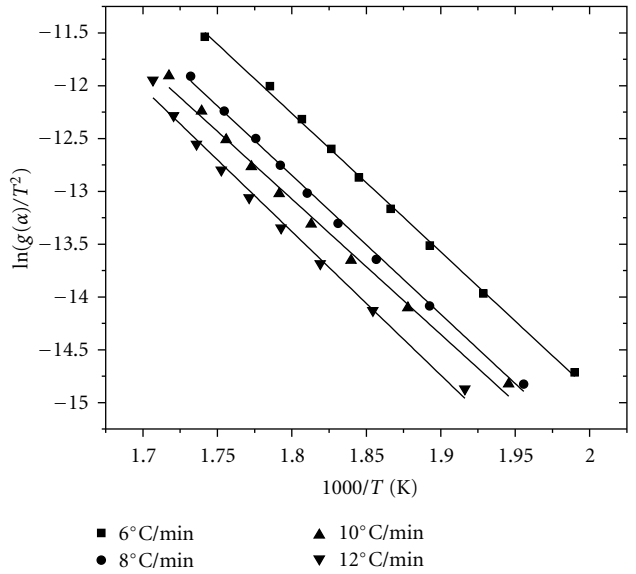

Figure 6: Redfern-Coats plot of $\ln[g(\alpha)/T^2]$ versus $1/T$; where $g(\alpha) = 2[1 - (1 - \alpha)^{1/2}]$.

energy values obtained from nonisothermal experiments are in good agreement with those values computed using the procedures of Arrhenius and Flynn-Wall methods. The activation energy obtained from isothermal experiment is found to be 87 ± 4 kJ/mol which was comparable with the enthalpy of sublimation value of 85 ± 4 kJ/mol. The activation energies derived from nonisothermal experiments at the lowest heating rate, and isothermal conditions were found to be on good agreement with each other, and it confirms the validity of the reaction mechanism deduced for each stage. The thermal degradation mechanism for $Zr(tmhd)_4$ system is a decelerated R_n type, which is a solid-state process based on contract volume (R_2). At the heating rate of 10°C/min, the activation energy is in good agreement with the decelerated method. Among these different techniques, the Arrhenius method is quite useful to study the energy of activation and it is useful for CVD applications.

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