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NON-ISOTHERMAL KINETIC AND THERMODYNAMIC PARAMETERS OF AMMONIUM PARATUNGSTATE DECOMPOSITION—A THERMOANALYTIC STUDY

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ABSTRACT

Non-isothermal kinetic (k, A and ΔE) and thermodynamic (ΔH, C_p and ΔS) parameters of ammonium paratungstate decomposition to the onset of formation of WO_3 were determined by analysing thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves recorded at various heating rates (1–30 °C min^{-1}). Thermal events encountered throughout the decomposition course were due to three endothermic (at 120 °C (I), 195 °C (II) and 359 °C (IV)) and two exothermic (at 265 °C (III) and 386 °C (V)) processes. The events I–IV were accompanied by weight losses resulting from the elimination of volatile components [$(NH_4)_2O$, NH_3 and H_2O] leading to the formation of intermediate solid products (metatungstate and polytungstate), whereas event V was due to the crystallization of WO_3 in the immediate vicinity of its formation (at 370 °C).

INTRODUCTION

Ammonium paratungstate (APT), a complex compound [$(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 7H_2O$] that crystallizes in space group *pbca* with a pseudo-symmetry $2/m$ [1], is frequently used as a precursor of supported and unsupported WO_3 catalysts [2]. An earlier thermoanalytic and spectroscopic investigation [3] performed in this laboratory has suggested a largely complete transformation of APT to WO_3 at about 370 °C via four weight loss steps maximized at 120 °C (endo), 195 °C (endo), 265 °C (exo) and 359 °C (endo). These steps were succeeded by a highly exothermic crystallization-process of WO_3 at around 386 °C. The physico-chemical identity of gaseous and solid materials produced via each step has been characterized as summarized in Table 1.

The present work, however, concerns kinetic and thermodynamic parameters of the various steps of APT decomposition to the onset of WO_3

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TABLE 1

Characteristics of thermal events encountered throughout the decomposition course of APT (at 5 °C min^{-1})

Thermal event	Temperature range (°C)	% Weight loss	Characteristics [a]
I	100–130	1.5	Elimination of surface CO_3^{2-} and HCO_3^- groups as well as a minute amount of $(NH_4)_2O$ species
II	190–210	2.0	Conversion of APT to ammonium metatungstate $[(NH_4)_5(H_2W_{12}O_{40})\cdot 7H_2O]$ with a simultaneous release of NH_3 and H_2O into the gas phase
III	240–290	6.5	Collapse of the polytungstate lattice leading to an amorphous substance, following complete loss of hydration water
IV	340–370	1.5	Formation of WO_3
V	≃ 386	–	Crystallization of WO_3

[a] As concluded earlier in ref. 3.

formation. The study was carried out by means of TG, DTA and DSC thermoanalytical techniques, under non-isothermal conditions. Despite occasional criticisms concerning the non-isothermal mode of kinetic studies [4], this approach has been adopted in this study because of the fact that fast reaction steps proceed to some extent during the heating process up to the desired temperature, thus making a precise kinetic analysis practically impossible.

EXPERIMENTAL

Materials and techniques

The ammonium paratungstate (APT) used was an AR-grade (> 99% pure) Fluka (Switzerland) product.

Thermogravimetric (TG), differential thermal (DTA) and differential scanning calorimetric analyses were performed with a Shimadzu Unit (Model-30H).

TG and DTA curves were recorded on heating up to 500 °C at four different heating rates (θ), standardized at 5 °C, 10 °C, 15 °C and 30 °C min^{-1} in a dynamic atmosphere of air (20 ml min^{-1}), using small portions of APT (10–15 mg). Highly sintered α-Al_2O_3 was used as a reference material for the DTA measurements. DSC data were recorded over the same range of temperatures, but at $\theta = 2\,^\circ C$, $5\,^\circ C$, $10\,^\circ C$ and $20\,^\circ C$ min^{-1}, and in a dynamic atmosphere of nitrogen (20 ml min^{-1}) to avoid oxidation of the calorimeter's copper cell-seats. The heat of transition (28.24 J g^{-1} [5]) of Specpure Indium metal (Johnson Matthey), at 157 °C, was adopted for the DSC curve calibration.

Data analysis procedure

Calculation of kinetic parameters

From the resultant thermoanalytical curves, the temperatures (T_{max}) at the maximum weight loss (TG) accompanying each of thermal events I–IV, or at the peak of the DTA curve corresponding to event V (the invariant weight process), were determined as a function of the heating rate (θ) applied.

The kinetic activation energy (ΔE J g^{-1}) was then calculated for each event from a plot of log θ vs. $1/T_{max}$, as interrelated by the following equation [6]

$$\Delta E = -\frac{R}{b\ \mathrm{d}\log\theta/\mathrm{d}(1/T)} \tag{1}$$

where R is the gas constant ($= 8.314$ J mol^{-1} °C^{-1}), θ is the heating rate (°C min^{-1}) and b is a constant ($= 0.457$).

Calculation of the frequency factor (A s^{-1}) of the decomposition reaction(s) involved in the thermal events (I–IV) was carried out, assuming a first-order kinetics, using the following equation [7]

$$\log[-\log(1-C)/T^2] = \log AR/\theta\,\Delta E - \Delta E/2.303RT \tag{2}$$

where C is the fraction decomposed and T is the T_{max}. Having been determined, ΔE (from eqn. (1)) and A (from eqn. (2)) were used to calculate the reaction rate constant (k min^{-1}) adopting the Arrhenius equation

$$k = A\ e^{-\Delta E/RT} \tag{3}$$

Calculation of thermodynamic parameters

The enthalpy (ΔH J g^{-1}) of all the thermal events encountered was directly determined from the DSC data (recorded at 5 °C min^{-1}) using the following equation [8]

$$\Delta H = \frac{60BCq_mA}{m} \tag{4}$$

where B is the time base (min in^{-1}), C is the cell calibration coefficient, q_m is the Y-axis sensitivity (J s^{-1} in^{-1}), A is the peak area (in^2) and m is the sample weight (g). ΔH thus determined was used to calculate the specific heat capacity (C_p J K^{-1} g^{-1}) using the equation: $C_p = \Delta H/\Delta T$, where $\Delta T = T_2 - T_1$, and T_1 is the temperature at which the DSC peak begins to leave the base line, whereas T_2 is the temperature at which the peak lands [9]. Subsequently, the entropy change (ΔS J K^{-1} g^{-1}) was calculated using the relationship $\Delta S = 2.303 C_p \log(T_2/T_1)$ [9].

RESULTS AND DISCUSSION

TG and DTA curves recorded for APT at 5 °C min^{-1} are shown in Fig. 1. The curves indicate that APT decomposes via four weight loss steps maximized at 120 °C (endo), 195 °C (endo), 265 °C (exo) and 359 °C (endo), ending up with a solid product that suffers an exothermic physical change centred around 386 °C. For convenience, these events are respectively termed I, II, III, IV and V, and their characteristics, as earlier revealed [3], are summarized in Table 1. Figure 2 and Table 2 show shifts of temperature T at which weight losses (TG) and peaks of corresponding DTA curves, respectively, are maximized, as a function of the heating rate ($\theta = 1$–30 °C min^{-1}) applied. Log θ vs. $1/T$ plots (Fig. 3) constructed for thermal events I–IV, on the basis of the TG results (Fig. 2), and for event V, on the basis of the DTA results (Table 2), were subsequently used to calculate the values of ΔE compiled in Table 3. Table 3 also compiles the corresponding k, log A, ΔH, C_p and ΔS values. The thermodynamic parameters ΔH, C_p and ΔS were calculated on basis of the DSC curve recorded at 5 °C min^{-1}, which is shown, together with the curves obtained at other heating rates, in Fig. 4.

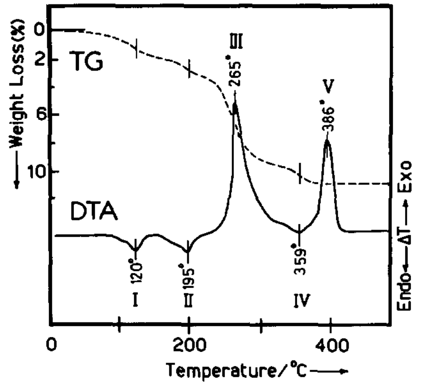

Fig. 1. TG and DTA curves recorded for APT at 5 °C min^{-1} in a dynamic (20 ml min^{-1}) atmosphere of air.

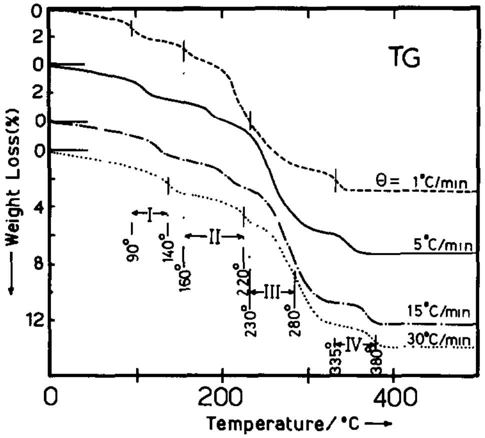

Fig. 2. TG curves recorded for APT at the heating rates (θ) indicated and in a dynamic (20 ml min^{-1}) atmosphere of air.

TABLE 2

Relationship between the heating rate and temperature (T_{max}) at the peak of DTA curves corresponding to the various thermal events (I–V) encountered throughout the APT decomposition course

Heating rate (°C min^{-1})	T_{max} (°C)				
	I (Endo)	II (Endo)	III (Exo)	IV (Endo)	V (Exo)
1	103	165	235	331	373
5	120	195	265	359	386
15	143	223	311	377	401
30	149	228	335	392	421

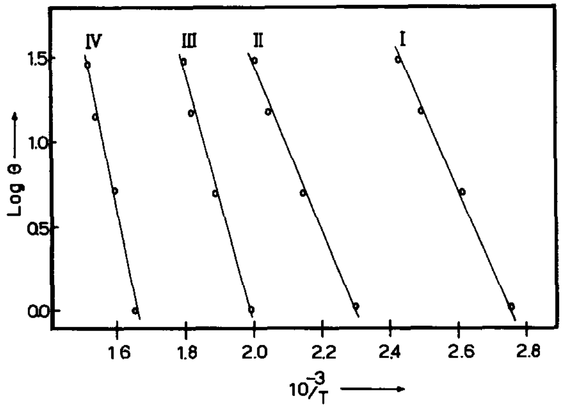

Fig. 3. Log θ vs. $1/T$ plots derived for the APT weight loss steps from the TG curves shown in Fig. 2.

TABLE 3

Non-isothermal kinetic [a] and thermodynamic [b] parameters of the thermal events encountered throughout the decomposition course of APT

Thermal event	k (min^{-1})	log A	ΔE ($\mathrm{J\,g}^{-1}$)	ΔH ($\mathrm{J\,g}^{-1}$)	C_p ($\mathrm{J\,g}^{-1}$ $\times 10^{-2}$)	ΔS ($\mathrm{J\,K}^{-1}\,\mathrm{g}^{-1}$ $\times 10^{-3}$)
I	1.166	14.37	40.5	–	–	–
II	0.933	13.85	41.0	1.70	2.83	3.88
III	0.773	12.19	44.9	2.45	6.44	4.78
IV	0.901	15.10	51.8	16.04	17.82	12.11
V	–	–	105.6	–3.45	9.08	–5.12

[a] Kinetic parameters of thermal event V were calculated from DTA data, whereas those of the rest (I–IV) were from TG data.

[b] Thermodynamic parameters were determined on the basis of DSC data recorded at 5 °C min^{-1}.

Thermal event I (100–130 °C)

This has been shown (Table 1) to involve a slight weight loss (1.5%) due to elimination of CO_3^{2-} and HCO_3^- surface contaminants together with a minute amount of $(NH_4)_2O$ species. The calculated kinetic parameters (Table 3) can infer that the weight loss occurs via fast, low-energy reactions. The corresponding enthalpy change escaped detection by the DSC analysis

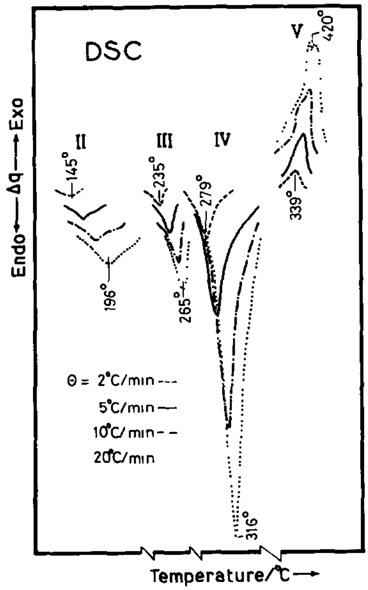

Fig. 4. DSC curves recorded for APT at the heating rates (θ) indicated and in a dynamic (20 ml min^{-1}) atmosphere of nitrogen.

(Fig. 4) even at the highest heating rate applied (20 °C min^{-1}), thus suggesting that much of it is associated with desorption, rather than a decomposition, of weakly bound species. In fact, an XRD analysis of APT calcined at 150 °C for 2 h resulted in a diffraction pattern almost identical with that of untreated APT [3]. Therefore, thermal event I can reasonably be considered to accompany a topochemical-type process that has insignificant impact on the structure and composition of the material.

Thermal event II (190–210 °C)

It has been found (Table 1) that this event involves the release of NH_3 and H_2O into the gas phase with a simultaneous transformation of the solid substance into ammonium metatungstate ($(NH_4)_5(H_2W_{12}O_{40}) \cdot 7H_2O$). XRD analysis has shown [3] that the metatungstate possesses a structure isomorphous with that of the paratungstate but with slightly larger *d*-spacings. Kinetically speaking, the reaction involved is slower than that which occurred in thermal event I, although of comparable A and ΔE values (Table 3). The corresponding, slightly positive enthalpy change (1.7 J g^{-1}), may suggest that the volatile constituents released (NH_3 and H_2O) have been driven off from weak linkages which have an insignificant contribution to the forces responsible for the polytungstate lattice coherency. However, the slightly positive entropy change (3.88×10^{-3} J K^{-1} g^{-1}) may indicate that the structure assumed by the metatungstate is less ordered.

A detailed structural analysis of APT [1] has disclosed that the paratungstate ion consists of four corner-sharing groups, each containing three edge-sharing WO_5 octahedra and that each ion is connected via NH_4^+ ions to ten others through bonds of different lengths. It has, moreover, been disclosed [1] that some of the NH_4^+ ions contain exchange interactions with some of the hydration water, thus contributing somewhat to the coherency of the lattice structure. Accordingly, it may be suggested that NH_3 release throughout thermal event II occurs mostly at the expense of these ions.

Thermal event III (240–290 °C)

Kinetically this event is shown to involve a decomposition reaction of lower k and A, and higher ΔE, ΔH and ΔS values than those calculated for the reaction involved in thermal event II (Table 3). Physico-chemically, event III has satisfactorily been found (Table 1 and ref. 2) to indicate the collapse of the polytungstate lattice resulting in a dehydrated, amorphous material retaining some NH_4^+ ions. It is obvious that we are now dealing with a fundamental decomposition process occurring with a mechanism different from the earlier two. It has been presumed [3] that the weight loss determined (6.5%) occurs at the expense of the NH_3 involved in cementing the polytungstate ions together, thus leading to the destruction observed and consequently to a further polymerization of the tungstate octahedra as an intermediate step on the way to the highest degree of polymerization attained by the WO_3 structure [10].

Thermal event IV (340–370 °C)

This represents the last weight loss step encountered prior to the formation of WO_3 (Table 1). The weight loss determined (1.5%) is, therefore, associated with the release of the remainder of the NH_3, to enable the necessary further polymerization to WO_3. The thermodynamic parameters (Table 3) reveal that the reaction involved is largely deceleratory (high ΔE), resulting in a highly disordered solid product (highly positive ΔS). The accompanying, remarkable increase in the enthalpy change (to 16.04 J g^{-1}) supports this.

Thermal event V (386 °C)

This event indicates a physical process (no weight change) that brings the system back to orderedness (ΔS becoming negative, see Table 3). It has been identified [3] as accompanying the crystallization of WO_3. The notably high ΔE value (105.6 J g^{-1}) conforms with the fact that this is a purely solid-state bulk process, where interactions at the gas–solid interface play a retrogressive role. On the other hand, the negative enthalpy change (-3.45 J g^{-1}) determined for the process may indicate spontaneity.

CONCLUSIONS

Ammonium paratungstate (APT) decomposes almost completely at 370 °C to give WO_3, which immediately crystallizes at 386 °C. TG analysis indicates that the weight loss experienced by APT on the way to WO_3-formation occurs in four steps maximized at 120 °C (I), 195 °C (II), 265 °C (III) and 359 °C (IV). The non-isothermal kinetic (k, A and ΔE) and thermodynamic (ΔH, C_p and ΔS) parameters determined indicate that the weight loss steps (I and II), occurring at ≤ 210 °C, take place with one and the same mechanism, and cause the least degree of disorder to the original structure. In contrast, the steps (III and IV), occurring at ≥ 240 °C, involve a different mechanism and lead to a radical change in the original structure and, consequently, to a maximum disorder. A succeeding exothermic process (V) with no weight change (at 386 °C) occurs through an ordering mechanism conducted with maximum kinetic activation energy.

The above kinetic and thermodynamic indications, together with previous (ref. 3 and Table 1) physico-chemical analyses of gaseous and solid products formed throughout the decomposition course, suggest that $(NH_4)_2O$, NH_3

and H_2O released during steps I and II are driven-off weakly-bound species of insignificant contribution to the overall coherency of the original lattice; whereas those eliminated during steps III and IV are driven-off binding species.

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