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SPECTROTHERMAL INVESTIGATION OF THE DECOMPOSITION COURSE OF LANTHANUM ACETATE HYDRATE

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Abstract

Thermogravimetry, differential thermal, X-ray diffraction and infrared spectroscopy analyses showed $La(CH_3COO)_3 \cdot 1.5H_2O$ to decompose completely at 700°C yielding La_2O_3. The results revealed that the compound dehydrates in two steps at 130 and 180°C, and recrystallizes at 210°C. Water thus produced hydrolyzes surface acetates (at 310°C), releasing acetic acid into the gas phase. At 334°C, the anhydrous acetate releases gas phase CH_3COCH_3 to give $La_2(CO_3)_3$ residue, which decomposes to $La_2O_2(CO_3)$ via the intermediate $La_2O(CO_3)_2$. On further heating up to 700°C, La_2O_3 is formed. IR spectroscopy of the gaseous products indicated a chemical reactivity at gas/solid interfaces formed throughout the decomposition course. As a result, CH_3COCH_3 was involved in a surface-mediated, bimolecular reaction, releasing CH_4 and C_4H_8 (isobutene) into the gas phase.

Non-isothermal kinetic parameters, the rate constant k, frequency factor A, and activation energy ΔE, were calculated on the basis of temperature shifts experienced in the thermal processes encountered, at various heating rates (2–20 deg·min^{-1}).

Keywords: kinetics, lanthanum acetate hydrate, spectrothermal investigation, TG-DTA

Introduction

The genesis of transition metal oxides has been studied extensively by a number of investigators [1–4]. However, rare earth metal oxides have received little attention.

The thermal decomposition of metal acetates is occasionally used as a means of preparing metal and metal oxide catalysts [2, 3], some of which are of industrial importance [2]. The characterization of the decomposition course enables the provision of adequate thermal conditions for producing a solid of specific properties. For instance, sintering must be avoided if the oxide is to be used as a catalyst or catalyst support [5] since in catalysis materials of high surface area are required [6].

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Lanthanum oxide, the final product of the decomposition course studied in the present investigation, finds numerous applications in various fields, especially as a catalyst [7] and as a support for metal [8] and metal oxide [9] catalysts. A thorough survey of the literature revealed that very little information exists [10, 11] about the decomposition course of lanthanum acetate hydrate (denoted LaAc). The results indicated intermediate steps involved in the decomposition of LaAc to the onset of formation of La_2O_3. These are: i) loss of crystallization water at 170°C, ii) a stepwise decomposition of the anhydrous product to lanthanum dioxycarbonate at 350–500°C, and iii) break-down of the lanthanum dioxycarbonate to produce lanthanum oxide at 780°C. However, no attention has been paid to the gas phase products, the kinetic parameters and the gas/solid interfacial reactions.

The present investigation was undertaken to explore the thermal decomposition course of LaAc and the chemical reactivity at the gas/solid interface. To accomplish these objectives: i) the decomposition course was investigated by thermogravimetry and differential thermal analysis, ii) kinetic parameters (k, A, ΔE) of the thermal processes thus monitored were non-isothermally determined, iii) analysis of solid phase products was carried out by IR-spectroscopy and X-ray diffractometry, and iv) IR gas phase spectra were taken of the environment of accumulating gaseous product, so as to simulate conditions of slow removal of these products.

Experimental

Lanthanum acetate hydrate (LaAc)

The LaAc used, $La(CH_3COO)_3\cdot 1.5H_2O$, Aldrich product (USA) of 99.9% purity. In view of the thermoanalytical results, solid-phase decomposition products were obtained by heating at certain temperatures in the range from 200 to 900°C for 1 h in a dynamic atmosphere of air (20 $ml\cdot min^{-1}$). For simplicity, the products are designated by the formula of the parent compound and the temperature applied. For example, LaAc(200), means the solid phase product of heating of LaAc at 200°C for 1 h.

Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of LaAc were performed with an automatic recording Shimadzu 30H analyzer (Japan). 20 mg portions of LaAc were used for TG, and highly sintered α-Al_2O_3 was the thermally inert reference material for the DTA measurements. TG and DTA curves were recorded on heating up to 1000°C at various rates ($\theta = 2, 5, 10$ and 20 deg·min^{-1}), in a dynamic atmosphere of air (20 ml·min^{-1}).

X-ray diffractometry (XRD)

X-ray powder diffractograms of LaAc and its calcination products were obtained by means of a model JSX-60 PA Jeol diffractometer (Japan), equipped with a source of Ni-filtered CuK$_\alpha$ radiation. For identification purposes, the diffraction patterns (I/I^0 *vs.* d-spacing (Å)) obtained were matched with relevant ASTM standard data [12].

Infrared spectroscopy (IR)

IR spectra of LaAc and its solid phase calcination products were obtained at a resolution of 5.3 cm^{-1}, over the frequency range from 4000 to 200 cm^{-1}, using a model 580B Perkin-Elmer double-beam spectrophotometer (U.K.). The spectra were taken of thin ($\leq$20 mg·cm^{-2}), lightly loaded ($\leq$1% by weight) KBr-supported discs of the samples.

Infrared identification of the gaseous decomposition products was done with the help of spectra (4000–600 cm^{-1}) taken of the gas surrounding a 0.5 g sample of LaAc heated at 10 deg·min^{-1} to various temperatures (100–400°C) for 10 min, in a specially designed IR-cell [13]. The cell was equipped with KBr windows, and evacuated to 10^{-2} torr for 5 min prior to recording the gas phase spectra. The cell backround spectrum was subtracted using an on-line Perkin-Elmer Data Station (model 3500).

Non-isothermal kinetic analysis of thermoanalytical data:

The temperatures ($T_{\max}$) at which weight-variant (TG) and invariant (DTA) processes have maximum rate were determined as a function of the heating rate (θ) applied. The kinetic activation energy (ΔE kJ·mol^{-1}) was then calculated for each process from a plot of log θ *vs.* $1/T_{\max}$, according to the following relationship [14]:

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

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

The frequency factor (A s^{-1}) for the weight-variant processes was calculated assuming first order kinetics, by means of the following equation [15]:

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

were C is the fraction decomposed and $T = (T_{max})$. ΔE (determined Eq. (1)) and A (from Eq.(2)) were used to calculate the rate constant (deg·min^{-1}) using the Arrhenius equation:

$$k = Ae^{\Delta E\,/\,RT} \tag{3}$$

Results and discussion

TG and DTA curves recorded for LaAc heated to 900°C at 20 deg·min^{-1}, are shown in Fig. 1. The curves indicate that LaAc decomposes via six endother-

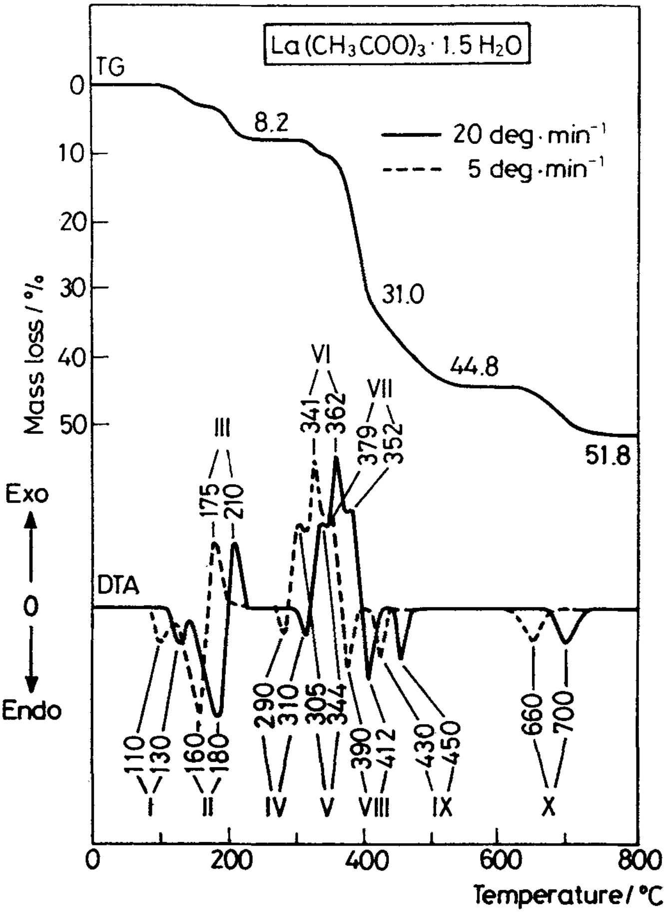

Fig. 1 TG and DTA curves recorded for LaAc, at the heating rates indicated, in a dynamic (20 ml min^{-1}) atmosphere of air

mic weight loss (WL) processes with maxima at 130 (I), 180 (II), 310 (IV), 412 (VIII), 450 (IX) and 700 (X), and three overlapping exothermic processes at 344 (V), 362 (VI) and 379°C (VII). Process II is followed by an exothermic weight invariant process III with maximum rate at 210°C.

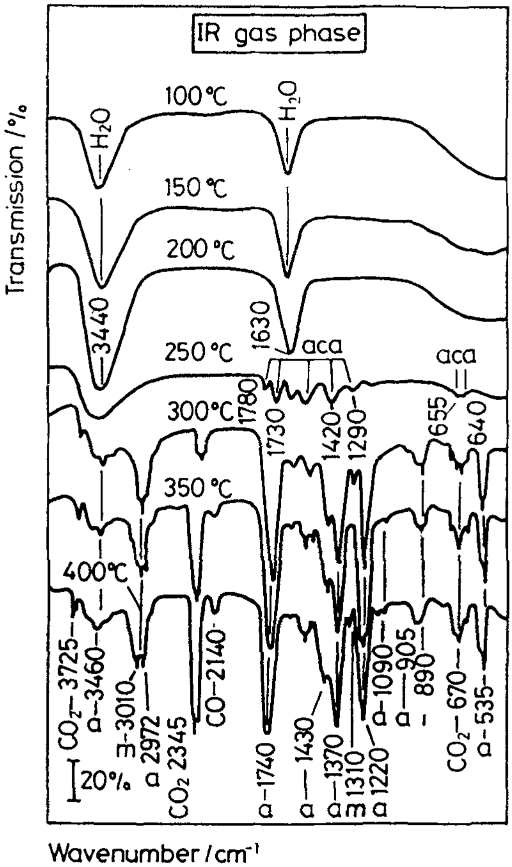

Fig. 2 IR spectra taken at a resolution of 5.3 cm^{-1} of the gas phase surrounding a 0.5 g portion of LaAc heated for 5 min. Gas-phase decomposition products indicated (*a* = acetone, *aca* = acetic acid, *m* = methane, *I* = isobutene).

Figure 2 exhibits IR gas phase spectra taken over the frequency range 4000–500 cm^{-1} of the atmosphere surrounding LaAc heated to various temperatures (100–400°C) for 10 min. However, IR spectra and X-ray powder diffractograms obtained for LaAc and its solid phase decomposition products at 200, 350, 600 and 900°C are shown in Figs 3 and 4, respectively.

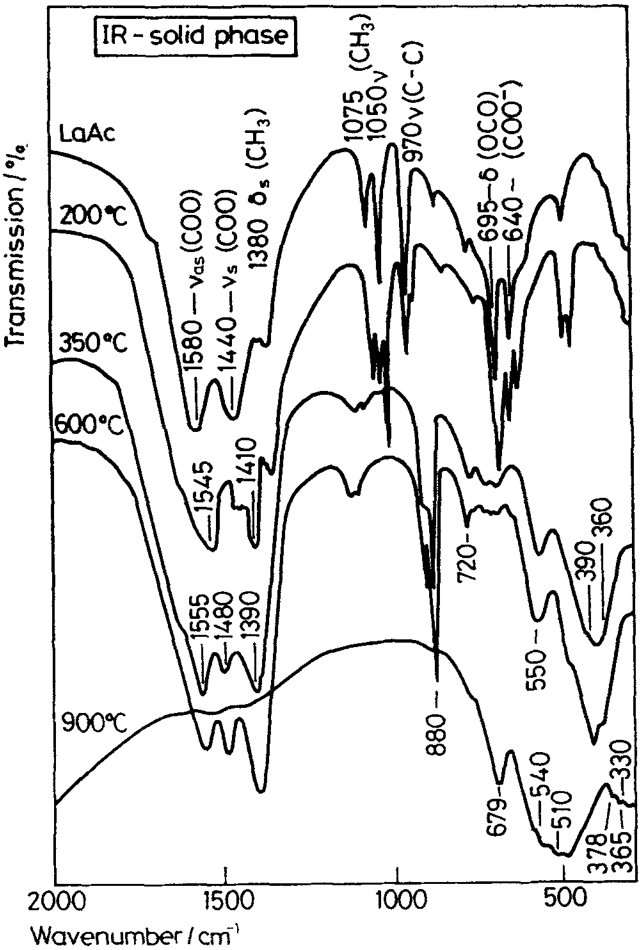

Fig. 3 IR spectra taken at a resolution of 5.3 cm^{-1} of KBr-supported samples of LaAc and its solid decomposition products obtained after heating at the temperature indicated for 1 h, in a dynamic atmosphere of air

Characterization of the thermal processes encountered

Processes I and II

The TG and DTA curves (Fig. 1) show that processes I and II are endothermic (WL) processes with maxima at 130 and 180°C, respectively. The total WL effected (8.2%) is very close to that expected (7.8%) for the release of 1.5 moles of water;

$$La(CH_3COO)_3 \cdot 1.5H_2O \rightarrow La(CH_3COO)_3 + 1.5H_2O \qquad (4)$$

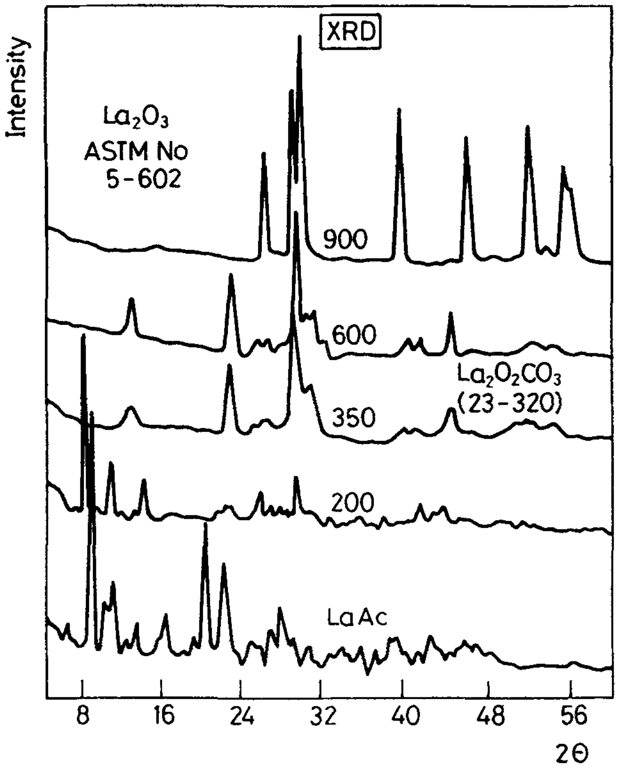

Fig. 4 X-ray powder diffractograms of LaAc and its decomposition products obtained after heating at the temperatures indicated for 1 h in a dynamic atmosphere of air

The corresponding activation energies (Table 1) have values of 53.50 (I) and 68.68 kJ·mol^{-1} (II), which are within the range characteristic of dehydration processes [1].

In support of the above results, the IR gas phase spectrum at 100°C (Fig. 2) displays a broad absorption centered around 3440 cm^{-1} and a strong absorption at 1630 cm^{-1}. These are due to ν(OH) and δ(HOH) vibrations of H_2O molecules respectively [16]. These absorptions are even more intense in the spectra taken at 150 and 200°C (Fig. 2).

Process III

Process III weight-invariant and exothermic; it has maximum rate at 210°C, i.e. immediately following the completion of the dehydration process II. The IR spectrum taken of the solid phase decomposition product at 200°C (Fig. 3) is similar to that exhibited by the untreated LaAc, in displaying almost all of the characteristic absorptions of acetate anions (at 1590–600 cm^{-1}) [17]. However,

Table 1 Non-isothermal kinetic parameters[a)] of the processes occurring throughout the decomposition course of LaAc

Process	k / min^{-1}	log$A$	ΔE / kJ·mol^{-1}
I	2.6×10^{-5}	13.94	53.50
II	1.1×10^{-5}	14.38	68.68
III	–	–	126.23
IV	0.8855	10.37	52.21
V	2.7×10^{-6}	10.26	118.05
VI	–	–	121.08
VII	–	–	152.29
VIII	3.6×10^{-10}	18.56	177.07
IX	4.6×10^{-11}	19.29	186.80
X	2.2×10^{-8}	17.40	218.00

[a)] The kinetic parameters for processes I, II, IV, V, VIII, IX and X were calculated from TG data, whereas for processes III, VI and VII, DTA data was used.

there are two detectable differences: (i) absorption due to the symmetric (ν_s) and antisymmetric (ν_{as}) vibrations of the carboxylic group are shifted in the spectrum of the product to lower frequencies than that of the parent material, and (ii) bands at 1057 (δ_{CH_3}), 970 ($\nu_{C\text{-}C}$) and 640 cm^{-1} ($\delta_{(COO)^-}$) split. These modifications may suggest a restructuring process of the acetate anions. The XRD pattern of LaAc(200) (Fig. 4) indicates a significant loss in crystallinity, following the dehydration of LaAc. The activation energy determined for process III is 126.26 kJ·mol^{-1}.

Process IV

Figure 1 shows that process IV causes a slight, endothermic (WL $\leq$ 3%) peak at 310°C. The gas phase IR spectrum at 250°C (Fig. 2) reveals the release of CH_3COOH vapour, as well as a significant drop in the intensities of the water absorptions at 3440 and 1630 cm^{-1}. These results may suggest that an acetate hydrolysis, restricted to the surface layers, is responsible for the release of CH_3COOH into the gas phase:

$$H_2O_{(g)} + CH_3COO^-_{(s)} \rightarrow CH_3COOH_{(g)} + OH^-_{(s)} \qquad (5)$$

where, g = gas and s = surface.

The acetate groups of the parent material are most probably bridge-bonded to the La ions, since the frequency difference between symmetric (ν_s) and antisymmetric (ν_{as}) vibrations of ($\Delta\nu_{COO^-}$) amounts to 140 cm^{-1} [17, 18]. The low frequency shifts experienced for these absorptions in the solid-phase IR spectra of LaAc(200) (Fig. 3) would indicate a weakening of acetate bonding to the metal atoms [3] on heating up to 200°C. Such a bond weakening seems to be responsible for making surface acetates liable to hydrolysis. Thus, one may consider process IV, which requires a low activation energy (52.2 $kJ\cdot mol^{-1}$), to pertain to the hydrolysis of surface acetates.

Processes V–IX

Processes V (344°C), VI (362°C) and VII (397°C) are exothermic, while processes VIII (412°C) and IX (450°C) are endothermic (Fig. 1). The strong overlapping of these processes is also clearly reflected in the TG curve (Fig. 1). This makes it difficult to explain on the basis of mass loss data. Nevertheless, the total mass loss (WL) effected (31.0%) at the observed kink near 350°C (processes V–VII) is close to that (31.4%) expected for the formation of $La_2(CO_3)_3$ from $La(CH_3COO)_3\cdot 1.5H_2O$:

$$2La(CH_3COO)_3\cdot 1.5H_2O \rightarrow La_2(CO_3)_3 + 3CH_3COCH_3 \qquad (6)$$

The next mass loss (WL) up to 44.8%, completed near 500°C, may correspond gravimetrically to the formation of $La_2O_2CO_3$:

$$La_2(CO_3)_3 \rightarrow La_2O_2CO_3 + 2CO_2 \qquad (7)$$

However, the two endothermic peaks at 412° (VIII) and 450°C (IX) indicate that the above process is composite in nature [19].

IR gas phase spectra obtained following heating at 300–400°C (Fig. 2), display characteristic bands due to acetone (at 1740, 1430, 1370 and 1220 cm^{-1}) [20], in support of reaction (6). Moreover, the simultaneous release of CH_3COCH_3 and CO_2 into the gas phase is consistent with the strong overlapping experienced for processes V–IX (Fig. 1). It also reveals that $La_2(CO_3)_3$ and the intermediate monooxycarbonate are thermally unstable, in agreement with the results reported by Moosath *et al.* [19]. These authors reported that during the decomposition of lanthanum oxalate hydrate, lanthanum carbonates were formed as intermediates with no region of stability.

In full agreement with the above discussion, the IR spectra taken of the solid phase product at 350 and 600°C (Fig. 3) show the disappearance of acetate absorption bands and appearance of absorptions assignable to oxycarbonate species (at 1555, 1480, 1390, 880, 720, 550, 390 and 360 cm^{-1} [20]). The XRD of the solid product at 350°C (Fig. 4) exhibits a pattern identical to that of $La_2O_2(CO_3)$ (ASTM No. 23–320). The crystallinity is shown to improve with increasing temperature up to 600°C. No other crystalline phases are observed in these patterns.

The activation energy has values of 118.50 (V) 121.08 (VI), 152.29 (VII), 140.00 (VIII) and 170.00 (IX) kJ·mol^{-1}.

Process X

The TG curve (Fig. 1) shows that process X takes place endothermally (DTA) at 700°C, with a mass loss (WL) (7.0%) that makes the total mass loss (WL) come up to 51.80%. It is now close to that expected (51.19%) for the decomposition of $La(CH_3COO)_3\cdot1.5H_2O$ to La_2O_3.

The XRD of the calcination product at 900°C (Fig. 4) only detects crystalline La_2O_3 (ASTM No. 5–602) which is hexagonal with one molecule in the unit cell in which La ions occupy D_{3d} site and the oxygen occupy C_{3v} and D_{3d} sites [20]. The IR spectrum of the same product (Fig. 3) reveals the disappearance of carbonate absorptions. It only displays absorption bands due to La_2O_3 (at 679, 554, 510, 430, 378, 360, 330 cm^{-1}) [20]. The kinetic parameters compiled in Table 1 for process X account for a slow reaction. The activation energy value (218.0 kJ·mol^{-1}) is higher than that (177.07 kJ·mol^{-1}) for process VIII and that (186.08 kJ·mol^{-1}) for process IX. Thus, $La_2O_2(CO_3)$ is more stable than $La_2(CO_3)_3$ and $La_2O(CO_3)_2$.

Reactivity at the gas/solid interface

The gas phase spectra at 350 and 400°C display absorption bands due to methane and isobutene; their positions are indicated in Fig. 2. These gases are not among the initial decomposition products of LaAc.

It has been shown earlier [3, 21, 22] that surface reactions of acetone over metal oxides can result in the formation of methane and isobutene. This has been attributed to a surface-mediated bimolecular reaction, in which acetone is adsorbed and, hence, activated for an aldol-condensation like process.

$$(CH_3)_2CO_{(s)} + OH^-_{(s)} + (CH_3)_2CO_{(g)} \rightarrow (CH_3)_2C = CH_{2(g)} + CH_3COO^-_{(s)} \quad (8)$$

In the meantime, adsorbed acetone is also activated for a nucleophilic attack by an adjacent surface OH$^-$ to split off a methyl group in the form of CH_4 [22];

$$(CH_3)_2CO_{(s)} + OH^-_{(s)} \rightarrow CH_{4(g)} + CH_3COO^-_{(s)} \quad (9)$$

It is to be noted that both reactions (8) and (9) occur at the expense of acetone. This may explain the decrease in the amount of acetone vapour commencing at 400°C (Fig. 2). This was made quite clear by increasing the temperature to 450°C.

Conclusions

The results of the present investigation allow the following conclusions to be drawn:

1) The thermal formation course of La_2O_3 from hydrated lanthanum acetate may include the following pathways:

$$La(CH_3COO)_3{\cdot}1.5H_2O \rightarrow La(CH_3COO)_3{\cdot}H_2O \rightarrow La(CH_3COO)_3 \rightarrow$$

$$La(CH_3COO)_3\ \text{(restructuring)} \rightarrow La_2(CO_3)_3 \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$$

2) Formation of acetone in the decomposition of LaAc rather than acetic acid is a typical behaviour of acetates of irreducible metal ions [23].

3) Reactions occurring at the gas/solid interfaces established throughout the decomposition course may help making useful conclusions concerning the catalytic behaviour of the associated solid products.

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Zusammenfassung — TG, DTA, Röntgendiffraktion und IR-Spektroskopie zeigen eine vollständige Zersetzung von $La(CH_3COO)_3 \cdot 1{,}5H_2O$ zu La_2O_3 bei 700°C. Die Ergebnisse zeigen, daß die Verbindung in zwei Schritten, bei 130 und bei 180°C dehydratiert und bei 210°C umkristallisiert wird. Das auf diese Weise entstehende Wasser hydrolisiert Oberflächenacetat (bei 310°C), wodurch Essigsäure in die Gasphase übergeht. Bei 334°C setzt das wasserfreie Acetat gasförmiges CH_3COCH_3 frei und ergibt $La_2(CO_3)_3$ als Rückstand, der sich über das Zwischenprodukt $La_2O(CO_3)_2$ zu $La_2O_2(CO_3)$ zersetzt. Durch weiteres Erhitzen auf 700°C wird La_2O_3 gebildet. IR-Spektroskopie der gasförmigen Produkte zeigt eine chemische Reaktivität an den wahrend des Zersetzungsweges gebildeten Gas/Feststoff-Phasengrenzen. Im Ergebnis wird Aceton in einer bimolekularen Oberflächenreaktion umgesetzt, wobei CH_4 und C_4H_8 (Isobuten) in die Gasphase abgegeben wird.

Nichtisotherme kinetische Parameter, die Geschwindigkeitskonstante k, der Frequenzfaktor A und die Aktivierungsenergie ΔE wurden anhand der Temperaturverschiebungen im thermischen Prozeß für verschiedene Aufheizgeschwindigkeiten (2–20 $deg \cdot min^{-1}$) berechnet.