Thermal decomposition of Yttrium(III) isovalerate in argon

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Abstract

The thermal behaviour of yttrium(III) isovalerate ($\text{Y}(\text{C}_4\text{H}_9\text{CO}_2)_3$) was studied in argon by means of thermogravimetry, differential thermal analysis, FTIR-spectroscopy, hot-stage optical microscopy and X-ray diffraction with a laboratory Cu-tube source as well as with a synchrotron radiation source. Two structural transitions take place in the solid state at 100°C and 140°C. They are followed by the decomposition of the isovalerate salt with release of gaseous products consisting of CO_2 and 2,6-dimethyl-4-heptanone and formation of $\text{Y}_2\text{O}_2\text{CO}_3$ between 320°C and 440°C. Above 440°C, $\text{Y}_2\text{O}_2\text{CO}_3$ is slowly converted to Y_2O_3 with release of CO_2 . The decomposition is complete at about 900°C.

Keywords: Yttrium isovalerate, thermal decomposition, TG-DTA, FTIR, carboxylates

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Introduction

Owing to its electronic properties, high stability and low cost, Y_2O_3 is emerging as a versatile material for a wide variety of applications such as sensors [1], catalyst supports [2], infrared converters [3], scintillators [4], lasers [5,6], bioimaging probes [7], purification systems [8], etc. Recently, Y_2O_3 was also found to be efficient for the planarization of Hastelloy tapes in view of the manufacture of second-generation high-temperature superconducting tapes [9]. The manufacture of Y_2O_3 thin films can be performed by various means, among which chemical solution deposition (CSD) appears as very attractive due to its low cost, ability to coat surfaces with complicated shapes and straightforward upscalability. Beside the manufacture of pure and doped Y_2O_3 coatings [10-13], CSD has also demonstrated its efficiency for making functional films combining other cations in association with yttrium, e.g. $(\text{Y},\text{Yb})\text{MnO}_3$ [11] and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [14-19].

The realization of high performance films with appropriate microstructure requires a very accurate control of the processing parameters, in particular during pyrolysis of the precursor, due to the interplay of several effects including solvent evaporation, dehydration, gas release, shrinkage, etc. For these reasons, a sound knowledge of the thermal decomposition mechanism of potential precursor salts is an asset. Previous studies have revealed that Y-based carboxylates behave differently upon heating depending on the nature of the involved ligands. For example, among the alkanoate compounds of Y studied so far: the formate [20], acetate [21], propanoate [22-25], butanoate [22] and pentanoate (valerate) [26], all decompose via a dioxymonocarbonate ($\text{Y}_2\text{O}_2\text{CO}_3$) intermediate, contrary to Y-heptanoate (enantate), which was reported to decompose directly to Y_2O_3 [27], while Y-hexanoate (caproate) was found to form the $\text{Y}_2\text{O}_2\text{CO}_3$ intermediate when decomposing in Ar [28] but not in air [29]. Melting of the anhydrous Y-alkanoates takes place only in compounds with relatively long ligands, i.e. butanoate, pentanoate

and hexanoate [22,26,28,29], although no melting was reported for Y-heptanoate [27]. Furthermore, evidence for the appearance of a transient oxoalkanoate phase with general formula $Y_2O(C_{2+n}H_{5+2n}CO_2)_4$ seems to be restricted to Y-alkanoates with relatively short ligands (acetate, propanoate, butanoate) [20,22]. Nevertheless, all these Y-alkanoates have in common the simultaneous evolution of CO_2 and a symmetrical ketone during their thermal decomposition.

Several other types of carboxylates such as Y-oxalate [21,30], tartrate [31], vanillate [32], 4-methoxybenzoate [33], etc. also form the $Y_2O_2CO_3$ intermediate phase but melting has not been observed in these salts.

The reported onset temperature for the decomposition of Y-carboxylates varies between 175°C [25] and 300°C [21-24,26]. However, a direct comparison of these values is difficult, because not all studies were conducted in inert atmosphere. The onset of decomposition is a very important parameter to define the stability of the salt if it is to be used as such; or its pyrolysis temperature if it needs to be decomposed. The occurrence of fusion as well as structure and viscosity of the molten phase are also crucial in view of possible applications of liquid crystal phases [34] as well as functional film processing [35]

To the best of our knowledge, no data are available in the literature on the thermal behavior of Y-isovalerate, and in fact of isovalerate complexes of metals, transition metals and rare-earth elements in general. In the present study it will be shown that the addition of a branched CH_3 group to the alkanoate backbone has some significant effects on the behavior of Y-isovalerate compared to that of the closely related Y-butanoate and Y-valerate compounds.

Experimental

The starting reagents consisted of $Y_2(CO_3)_3 \cdot 4H_2O$ from Alfa Aesar with 99.9 % purity (rare earth basis). 200 mg of this salt were dissolved in 4 ml isovaleric acid (IUPAC name 3-

methylbutanoic acid ($\text{C}_5\text{H}_{10}\text{O}_2$) from Alfa Aesar, 98 %). After keeping the solution at 50 °C for 2 weeks in order to evaporate the excess acid, a white solidified mass that could be easily ground into powder was obtained and used without additional treatment.

Simultaneous Thermogravimetry and Differential Thermal analysis (TG-DTA) measurements were performed in a model STA 449C from Netzsch at a heating rate of 5 °C/min up to 1250°C under argon flow (0.5 ppm residual O_2) at normal pressure, with a flow of 40 ml/min. The crucibles (6 mm diameter and 3 mm depth, i.e. 85 μl) consisted of alumina. Buoyancy corrections were applied based on data recorded on empty crucibles but otherwise similar experimental conditions. For the measurements, the sample mass was of 11.5 ± 0.3 mg. The powders were not compacted. $\alpha\text{-Al}_2\text{O}_3$ powder (48 mg) was used as reference.

A Bruker Tensor 27 spectrometer coupled to the exhaust line of the TG-DTA device by a transfer line heated to 200°C was used for obtaining Fourier transform infra-red (FTIR) spectra. FTIR spectra were also recorded on samples heated in the TG-DTA at a rate of 5 °C/min and air quenched by opening the furnace in order to examine the evolution of the decomposition products. High-temperature x-ray diffraction measurements up to 500°C were conducted at the Wiggler beamline BW5, located at the storage ring DORIS at DESY in Hamburg (Germany). The photon energy of the incident beam was 77.8 keV, corresponding to a wavelength $\lambda = 0.159$ Å. The diffraction patterns were recorded when warming the sample with heating rate of 5 °C/min in an Ar-filled furnace. More details on the experimental set-up and data analysis can be found in previous publications [36,37]. An X-ray diffraction (XRD) pattern was collected in a MD-10 bench-top X-ray diffractometer with $\text{CuK}\alpha$ radiation (position sensitive detector: $19^\circ \leq 2\theta \leq 70^\circ$) on a sample heated to 1400°C at a heating rate of 5°C/min under Ar flow in the TG-DTA and cooled at a rate of 50°C/min. The room temperature XRD pattern of the as-prepared Y-

isovalerate powder was recorded in a Rigaku SmartLab X-ray diffractometer also with $\text{CuK}\alpha$ radiation and the space group as well as the lattice parameters were determined by means of the PDXL2 software. The evolution of microstructural features was observed at low magnification (50x) by hot-stage optical microscopy up to 800°C under Ar flow in a HCP901 chamber from INSTEC Ltd calibrated by observing the melting of metal standards (In, Sn, Bi, Zn and Al).

Results and discussion

The FTIR spectrum of the as-prepared Y-isovalerate sample is shown in Fig. 1. It exhibits absorption bands similar to those of Na-isovalerate [38]. A tentative assignment of the absorption bands has been made by comparison with the spectra of Y-valerate [26] and Y-butanoate [22]. A list of the identified absorption bands with their assignments is provided in supplementary file S1. The strong band at 1541 cm^{-1} is due to the asymmetric carboxyl stretching ($\nu_{\text{as}}(\text{COO}^-)$) vibrations, whereas the symmetric carboxyl stretching band ($\nu_{\text{s}}(\text{COO}^-)$) occurs at 1411 cm^{-1} . The $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ value is 130 cm^{-1} for yttrium isovalerate and thus slightly smaller than for Na-hexanoate [38]. According to the study of Deacon and Phillips [39], it could be concluded that bidentate chelating or bridging coordination is present in Y-isovalerate, similarly to the cases of Y-hexanoate [28] and Y-valerate [26].

The room temperature XRD pattern of the Y-isovalerate powder is also presented in Fig. 1. It is characterized by three strong lines at low scattering angles ($2\theta < 12^\circ$). However, the corresponding d-spacings do not differ by simple ratios as would be expected if the crystal structure of Y-isovalerate was built simply on planes of Y atoms interleaved by the ligands, like in the cases of many rare-earth alkanoates [40-45]. Instead, indexing of the XRD pattern (see supplementary file S2) indicates that the compound crystallises in the monoclinic space group P2/m (10) with the following cell parameters: $a = 2.352 \text{ nm}$, $b = 1.637 \text{ nm}$, $c = 2.009 \text{ nm}$ and $\beta =$

110.5°. A full determination of the crystal structure was unfortunately not possible on the basis of the powder diagram of this sample and will probably require single crystals.

Figure 2 shows the DTA, TG and DTG traces recorded at a heating rate of 5 °C/min. The low temperature range of the DTA trace is characterized by two sharp endothermic peaks with onsets at 100°C and 140°C (I and II in Fig. 2) that are not associated to mass losses. The in-situ XRD patterns (Fig. 3) show that they correspond to structural phase transitions. The patterns at 25°C and 99°C exhibit the same diffraction lines that only move to lower scattering angle with increasing temperature as a result of thermal dilatation. In contrast, the pattern recorded at 112°C shows different lines, which survive up to 138°C and are again replaced, at 147°C, by a new type of pattern including a high intensity line in the low angle range of the pattern. Besides a shift of the lines towards lower scattering angles, this diffraction pattern remains unchanged up to about 400°C and then vanishes as the temperature is further increased. Both Y-butyrate and Y-valerate presents a single endothermic reaction in the same temperature range (105°C and 90°C respectively) [22,26]. These features were found to correspond to melting and resulted in the loss of crystallinity. The situation appears to be different for Y-isovalerate. In order to check if a liquid crystalline phase had formed as is the case in Y-butyrate [22] and Y-valerate [26], the morphology of Y-isovalerate powders was examined by means of hot-stage microscopy. As the pictures shown in Fig. 4 demonstrate, there is no evidence for melting in the temperature range corresponding to the endothermic peaks I and II in this compound. However the powders shrink to some extent up to about 300°C, probably as a result of the structural phase transitions.

It should be noted that a very slight mass loss occurs starting from about 150°C, i.e. at a temperature a little larger than that of the DTA peak II. The fact that this mass loss takes place after the end of the endothermic reaction indicates that it is not due to a decomposition reaction

taking place in the compound and resulting in the simultaneous evolution of a gaseous product of decomposition. We assume that this loss may be due to sublimation of Y-isovalerate. Another possible explanation might have been that some residual isovaleric acid evaporated at $T \geq 150^{\circ}\text{C}$ (boiling point = 175°C), but this hypothesis can be discarded, because a mass loss with the same intensity and rate was observed if the sample was evacuated at room temperature for 24 h or shortly heated to 200°C prior to measurement. The reversibility of the reactions responsible for the DTA peaks I and II was also assessed by performing thermal cycles between room temperature and 200°C with a heating rate of $5^{\circ}\text{C}/\text{min}$. The results are shown in Fig.2d. Upon cooling after a first heating up to 200°C , two exothermic peaks appear at temperatures lower than those of the endothermic peaks found during heating, indicating that undercooling takes place to some extent (about 30°C for both reactions). During the second heating, the two endothermic peaks appear again. While peak I is shifted to a slightly higher temperature, peak II appears at exactly the same temperature as during the first heating cycle. The exothermic features appearing during subsequent cooling (2nd cooling) are very similar to those observed during the 1st cooling.

Fig.5 shows details of the *in-situ* XRD patterns during the main mass loss linked to DTA peak III. Whereas the low angle region shows that Y-isovalerate is still clearly present up to 426°C , it clearly coexists with a new phase characterized by XRD peaks appearing already around 400°C in the higher angle region of the XRD patterns. These peaks are rather broad, indicative of a nanocrystalline structure and can be assigned either to Y_2O_3 or to $\text{Y}_2\text{O}_2\text{CO}_3$ [46]. Fig.6, which presents the FTIR spectra recorded on the solid residue remaining in the TG-DTA crucibles after heating to various temperatures from 410°C to 440°C and air quenching, reveals that $\text{Y}_2\text{O}_2\text{CO}_3$ is present and that the last traces of the isovalerate ligands, characterized by the ν_{as} and ν_{s} vibrations of the CH_2 and CH_3 groups at 2850 cm^{-1} – 3000 cm^{-1} have disappeared at 440°C . At

this temperature, the overall mass loss amounts to 65.4%, which is quite close to the 65.6% theoretically expected for the decomposition of $Y(C_4H_9CO_2)_3$ to $Y_2O_2CO_3$ with release of the other decomposition products in gaseous form. During this transformation, the powder further shrinks and a dark shade appears (Fig.4), indicating that some carbonaceous residue is left in the powder, as will be discussed later.

It is remarkable that the sample does not become amorphous up to the decomposition temperature. This means that Y-isovalerate does not form an isotropic liquid phase upon heating, in contrast to the case of Y-butyrate [22] and Y-valerate [26] and shows that the presence of a branched methyl group can effectively suppress melting and the complete loss of long-range order upon heating.

As shown in Fig. 7, the gas species evolving during the thermal event III include CO_2 and a ketone, which can be identified as 2,6-dimethyl-4-heptanone as shown by the excellent correspondence of the progression bands with a reference pattern for this compound [47]. The decomposition reaction corresponding to this reaction step can therefore be described as:

This decomposition starts around 320°C, which is higher than the onset decomposition temperature of Y-butyrate and Y-valerate ($\approx 290^\circ C$) under similar experimental conditions [22,26], demonstrating an enhanced thermal stability for Y-isovalerate.

Between 450°C and 550°C, two low intensity features denoted as IV and IV' in Fig.2 appear in the DTA trace. It is at first sight not clear whether IV is an independent endothermic event ending at $\approx 505^\circ C$ (maximum of the exothermic upturn IV') or if it consists of the onset of the large endothermic peak V developing up to 900°C, upon which an exothermic reaction (peak

IV') is superimposed. Fig.8 shows the FTIR spectra of the solid residues remaining in the TG-DTA crucibles after heating to 500°C and 550°C, i.e. before and after the DTA feature IV'. It can be noted that the spectrum of the sample quenched from 500°C is similar to that shown in Fig.6 for a sample quenched from 440°C, and that no changes are observed after the end of peak IV' (550°C). On the other hand, optical microscope images of the solid decomposition residue (inset in Fig.8) reveal a significant modification of coloration between 500°C and 550°C. In this temperature range, only CO₂ evolution is recorded by FTIR (Fig.7). A possible interpretation for these observations is that the DTA feature IV' is actually an exothermic reaction consisting in the oxidation, by the trace oxygen present in the carrier gas, of some carbonaceous residue formed in the sample during the decomposition of Y-isovalerate.

Reaction (1) does not account for the formation of elemental carbon. However, it is possible that besides the main reaction path (1), recombination of some acyl units can also take place and result in the formation of 2,5-dimethylhexane (C₈H₁₈), CO₂ and elemental C according to reaction (2):

While, two alkyl radicals can combine to form also 2,5-dimethylhexane without other educts:

2,5-dimethylhexane (C₈H₁₈) must be released as a gas species simultaneously with the gaseous products of reaction (1). Unfortunately, the FTIR spectrum of 2,5-dimethylhexane strongly overlaps with that of 2,6-dimethyl-4-heptanone so that a minute amount of the former cannot be detected. Assuming that reaction (2) takes place to some extent, it is most probable that the DTA feature IV is in fact merely the initial part of the broad endothermic peak occurring between up

to 900°C (V in Fig 2). This peak is accompanied by CO₂ evolution (739°C in Fig. 7) and the final decomposition product consists of Y₂O₃ as shown by the XRD pattern and FTIR spectrum of the powder left in the crucible after heating to 1400°C (Fig.9). The thermal event V is therefore linked to the final thermal decomposition of Y-dioxymonocarbonate into Y₂O₃ and CO₂:

The total experimental mass loss amounts to 71.1 % and is thus in excellent agreement with the theoretical value expected for the decomposition of Y-isovalerate to Y-sesquioxide (71.2 %). Generally, the thermal decomposition of Y-isovalerate follows a path similar to that of the Y-alkanoates studied so far. In particular, the evolution of the ketone 2,6-dimethyl-4-heptanone shows that the ligands do not undergo demethylation. If such had been the case, the ketone decomposition product would have probably been 4-heptanone for complete demethylation or 2-methyl-4-heptanone in case of partial demethylation only, leading to the formation of an Y-butanoate based intermediate product. These compounds are however not detected in the FTIR spectra, neither as evolved gas species, nor in the solid residues.

Finally, it is worth noting that the combination of two acyl radicals released during the carboxylate to oxycarbonate transformation stage was already mentioned in the thermal decomposition of Y-hexanoate and in that case it was possible to detect the presence of decane (C₁₀H₂₂) as a slight enhancement of some overlapping FTIR absorption peaks in the evolved gas spectrum. It would be interesting to see if more complex ligands result in an enhancement of this type of side reaction.

Conclusions

The thermal behaviour of Y-isovalerate $Y(C_4H_9CO_2)_3$ was studied during heating in Ar atmosphere at a rate of 5 °C/min. After two structural transitions that appear to take place in the solid state, Y-isovalerate decomposes into a symmetrical ketone: 2,6-dimethyl-4-heptanone as well as $Y_2O_2CO_3$ and CO_2 according to:

Some carbonaceous residue is formed by a side reaction. A tentative explanation is that the mechanism for this feature involves the combination of two acyl radicals formed during the decomposition of $2Y(C_4H_9CO_2)_3$ according to the free-radical mechanism:

However, overlap of the C_8H_{18} (2,5-dimethylhexane) FTIR absorption bands with the main absorption bands of $C_9H_{18}O$, which is released in the same temperature interval, prevents a confirmation of this reaction, which must be considered as an hypothesis.

The main decomposition reaction is followed by the decomposition of yttrium monoxycarbonate:

Contrary to the closely related Y-butanoate and Y-valerate salts, no melting takes place from a solid crystalline phase to an isotropic liquid phase. This could be advantageous for the manufacture of thin films, because the film morphology will not be disturbed by the formation of bubbles during the release of decomposition gasses. Furthermore, the decomposition starts at a higher temperature than for Y-butanoate and Y-valerate, revealing an enhanced stability brought about by the addition of a branched CH_3 group.

Acknowledgements

This work was supported by the Department of Energy Conversion and Storage, (project nr. 49605 E-5). The authors also acknowledge financial support from DANSCATT as well as DESY (project I-20110113 EC) for granting beamtime.

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Figure captions

Figure 1: XRD pattern with CuK α radiation, $\lambda = 1.54 \text{ \AA}$ (main frame) and FTIR spectrum (inset) of the as-prepared Y-isovalerate sample.

Figure 2: DTA (a), TG (b) and DTG (c) traces of Y-isovalerate heated in Ar at a rate of $5^\circ\text{C}/\text{min}$. DTA traces ($5^\circ\text{C}/\text{min}$) of Y-isovalerate during 1st cooling after heating up to 200°C , 2nd heating to 200°C and 2nd cooling to room temperature (d).

Figure 3: Low 2θ range of *in-situ* high energy (synchrotron, $\lambda = 0.159 \text{ \AA}$) XRD patterns recorded at various temperatures on Y-isovalerate powders during heating at $5^\circ\text{C}/\text{min}$ in Ar flow.

Figure 4: Hot stage optical microscope pictures captured at various temperatures on Y-isovalerate powders heated at $5^\circ\text{C}/\text{min}$ under Ar flow.

Figure 5: Low and high 2θ ranges of *in-situ* high energy (synchrotron $\lambda = 0.159 \text{ \AA}$) XRD patterns recorded at various temperatures on Y-isovalerate powders during heating at $5^\circ\text{C}/\text{min}$ in Ar flow.

Figure 6: FTIR spectra of the solid residue quenched from various temperatures during heating at $5^\circ\text{C}/\text{min}$ in Ar flow. The starting sample consisted of Y-isovalerate. The arrows show the absorption bands of $\text{Y}_2\text{O}_2\text{CO}_3$ [45]. Inset: detail of the $3100 - 2750 \text{ cm}^{-1}$ range evidencing the vanishing of typical ligand absorption bands.

Figure 7: Main frame: FTIR spectra of the gas phase evolving at various temperatures during the decomposition of Y-isovalerate. Open circles: CO_2 , filled circles: 2,6-dimethyl-4-heptanone. Inset: comparison of experimental data (solid line) with reference data from [46] (dots) between 1900 cm^{-1} and 750 cm^{-1} .

Figure 8: FTIR spectra of the solid residue quenched from 500°C and 550°C during heating at 5°C/min in Ar flow and optical microscope images of the same samples.

Figure 9: Main frame: XRD pattern of a sample heated to 1400°C and fast cooled. Inset: FTIR spectrum of the same sample showing the signature of Y_2O_3 and the complete disappearance of the $\text{Y}_2\text{O}_2\text{CO}_3$ absorption bands.