Journal of Analytical and Applied Pyrolysis 126 (2017) 77–87

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Thermal behavior and decomposition of cerium(III) butanoate, pentanoate and hexanoate salts upon heating in argon

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ARTICLE INFO

Keywords:
Cerium
Butyrate
Valerate
Caproate
Thermal decomposition
CeO_2

ABSTRACT

The thermal behavior and decomposition of Ce-butanoate monohydrate ($Ce(C_3H_7CO_2)_3{\cdot}H_2O$), Ce-pentanoate ($Ce(C_4H_9CO_2)_3$) and Ce-hexanoate ($Ce(C_5H_{11}CO_2)_3$) were studied in a flow of argon while heating at 5 °C/min. By means of several techniques such as simultaneous TG-DTA, FTIR evolved gas analysis, in-situ x-ray diffraction using a synchrotron source and hot-stage microscopy, it was found that all three compounds undergo melting transitions prior to decomposition and that decomposition involves intermediate stages including at least a $Ce_2O(C_nH_{2n+1}CO_2)_4$ intermediate (n = 3, 4 or 5 for Ce-butanoate, pentanoate or hexanoate respectively). The final decomposition product consists of CeO_2, which is formed through a Ce-oxycarbonate. The $Ce^{3+} \rightarrow Ce^{4+}$ oxidation seems to proceed via Ce_2O_3 that first results from the decomposition of the oxycarbonate phase. During the whole decomposition process, the evolved gas species consist of CO_2 and symmetrical ketones.

1. Introduction

Due to its outstanding properties, CeO_2 has tremendous potential for exploitation in various fields including biomedical applications (biosensing, immunoassay, drug delivery, radiation protection, tissue engineering, ophthalmology, implant coatings and antioxidant usage) [1–6], photocatalysis [7], steam reforming [8], preferential oxidation of impurities and pollutants (CO [9], SO_2, NO_x [10]), fuel cells and automotive applications [11], buffer layer coatings for superconducting tapes [12,13], etc.

The synthesis of CeO_2 nanoparticles and/or coatings can be achieved via different routes such as solvothermal [14], hydrothermal [15], precipitation [16–18] or thermal decomposition of complex precursors [19–21]. For the application of the latter technique, a good knowledge of the decomposition process is highly advantageous in order to control the morphology of the coating or nanoparticles as well as for ensuring safety during large scale handling due to the evolution of potentially toxic gases. Numerous studies have been published on the thermal decomposition of various cerium carboxylate salts as will be discussed in Section 3.4. Among this class of metalorganic compounds, the linear chain alkanoates have received limited attention. Besides cerium formate [22,23] and cerium acetate [24,25], the thermal decomposition of longer chain cerium alkanoates is limited to a few studies on cerium propionate [26,27], butanoate [28], pentanoate [29], hexanoate [30] and octanoate [30] performed under various conditions that do not allow systematic comparisons. Besides, there are some older works on Ce-laurate, palmitate and stearate [31] as well as hexanoate [28] that are based solely on thermogravimetric data with poor resolution (one point every 20 °C), from which limited information can be obtained. The aim of the present work was to systematically study the thermal decomposition of cerium butanoate, pentanoate and hexanoate under fixed conditions to study their thermal behavior, find similarities as well as differences between them and compare the results with those previously published on other cerium carboxylates and rare-earth butanoates, pentanoates and hexanoates.

2. Experimental

200 mg aliquots of $Ce_2(CO_3)_3{\cdot}xH_2O$ (x ≈ 4) from Alfa Aesar (99.9% purity (rare earth basis)) were dissolved separately in excess (4 ml)

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http://dx.doi.org/10.1016/j.jaap.2017.06.022
Received 7 March 2017; Received in revised form 21 June 2017; Accepted 22 June 2017
Available online 27 June 2017

butanoic acid (Alfa Aesar, 99 +%, common name: butyric acid), pentanoic acid (Alfa Aesar, 99%, common name: valeric acid) or hexanoic acid (Alfa Aesar, 98+ %, common name: caproic acid). After slow evaporation at room temperature for the solution in butanoic acid or 60 °C for the other two solutions during several weeks without stirring, a hard, yellow, transparent layer had formed on the bottom of the glass beakers. This mass was mechanically extracted and crushed into powders that were used without further treatment for characterisation and for the thermal decomposition studies.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) traces were acquired in a STA 449C Netzsch device at a heating rate of 5 °C/min up to 1000 °C in an argon flow of 40 ml/min at atmospheric pressure. Al_2O_3 (alumina) crucibles with 6 mm diameter and 3 mm depth were used. Buoyancy corrections were performed using background data recorded on empty crucibles under the same experimental conditions. A sample mass of 11.5 ± 0.2 mg was used for all measurements. The powders were not compacted. α-Al_2O_3 powder (46 mg) was used as reference.

Evolved gas analysis was performed by recording Fourier transform infrared (FTIR) spectra with a Bruker Tensor 27 spectrometer linked to the exhaust of the TG-DTA instrument by a transfer line maintained at 200 °C to minimize condensation of volatile decomposition products. FTIR spectra were also recorded on samples heated in the TG-DTA apparatus at a rate of 5 °C/min and air quenched by opening the furnace in order to follow the evolution of the decomposition products. High-temperature hard x-ray (synchrotron) diffraction measurements up to 560 °C were conducted at the Wiggler beamline BW5, located at the storage ring DORIS at DESY in Hamburg (Germany). The diffraction patterns were recorded during a temperature ramp of 5 °C/min with Ar flow in a dedicated furnace. The photon energy of the incident beam was 100 keV, corresponding to a wavelength λ = 0.124 Å. Details on the experimental setup and data analysis can be found in previous publications [32,33]. The advantage of using high-energy X-rays over a conventional laboratory X-ray source for this in-situ study is that the exposure time for each complete pattern can be as short as one second, thus avoiding averaging over a large temperature interval. The evolution of microstructural features was observed in-situ at low magnification (50x) by hot-stage optical microscopy up to 600 °C with a heating rate of 5 °C/min under Ar flow in a HCP901 chamber from INSTEC Ltd calibrated by observing the melting of metal standards (In, Sn, Bi, Zn and Al).

3. Results and discussion

3.1. Ce-hexanoate

The FTIR spectrum of the dried powder is shown in Fig. 1. It includes all the absorption bands previously observed in Ce-hexanoate [34], Y-hexanoate [35] and La-hexanoate [36], while the characteristic strong absorption bands for Ce-acetate at 1017 cm^{-1} and 1054 cm^{-1} [37] are not apparent, which allows concluding that the obtained compound consists of Ce-hexanoate. This is further supported by the similarity of the XRD pattern features (31 °C in Fig. 2) with those of La-hexanoate [36] as well as by the good fit between the theoretical mass loss corresponding to the decomposition of Ce-hexanoate into CeO_2 (64.5%) and the experimental result of thermal decomposition (64,0%) as will be shown in the following. The absence of a broad FTIR band between 3500 cm^{-1} and 3000 cm^{-1} indicates that the Ce-hexanoate salt has been obtained in the anhydrous state (Fig. 1). The separation between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ absorption bands ($\Delta\nu(COO)$) amounts to 131 cm^{-1}. This value is in the same range as for the cerium alkanoates investigated by Marques et al. [39] and Jongen et al. [40]. It is on the other hand smaller than for the ionic Na-hexanoate compound (145 cm^{-1}) [41]. According to Deacon and Phillips [42], this points to bidentate chelating but more than a single coordination type might be present as discussed in [40].

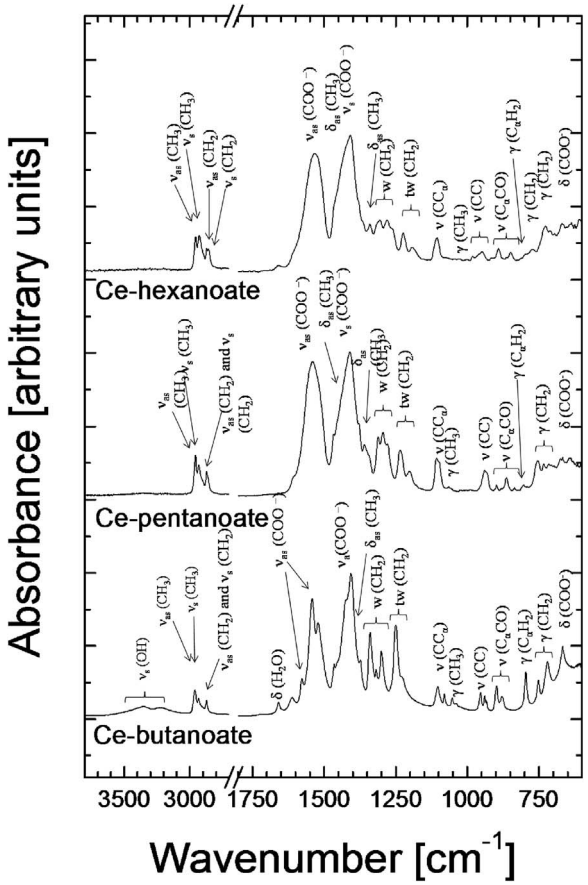

Fig. 1. FTIR spectrum of the as-prepared Ce-hexanoate, Ce-pentanoate and Ce-butanoate samples with band assignments based on [35,36,38,46].

Fig. 3 shows the DTA, TG and DTG traces of Ce-hexanoate powders. In the low temperature part of the DTA trace (T < 200 °C), two endothermic features, noted I and II, are visible with minima at 112 °C and 157 °C respectively. The first of those appears in the same temperature range as the dehydration endothermic peak observed by Brzyska and Paszkowska [30] upon heating $Ce(C_5H_{11}CO_2)_3{\cdot}2H_2O$ in air. However, since the FTIR spectrum of our starting sample does not show the presence of absorption bands related to H_2O, the endothermic peak I visible in Fig. 2a must be related to another cause. It more probably corresponds to a liquid crystalline phase transition reported by Jongen et al. [40] for the same compound. The hot-stage optical micrographs presented in Fig. 4 show that the microstructure of the powder has not significantly changed between before and after the first endothermic peak (images at 40 °C, 130 °C and 140 °C), but it looks more shiny and the particles are no more opaque, albeit not totally transparent after the endothermic event I. In-situ synchrotron data reveal a simultaneous structural change taking place in the same temperature interval, as shown in Fig. 2 (diffraction patterns at 105 °C and 122 °C). The sample is still crystalline, but the diffraction peaks have moved to higher 2θ values, suggesting a decrease of the lattice parameters. This is in accordance with the observations reported in [40] for the Ce $(C_nH_{2n+1}COO)_3$ $5 \le n \le 17$ series of Ce(III) alkanoates, where it is proposed that some kind of folding takes place in the alkyl chains, whereas the coherence of the lamellar bilayer structure based on planar Ce(III) ions layers is maintained. This transition could be a solid to smectic phase change according to the typical shift of the most intense diffraction peak that can be linked to the corresponding decrease of the interplanar lattice parameters. This is the only phase transition that could be evidenced in this sample between room temperature and 130 °C, in contrast to the report of Jongen et al. [40], who mention an additional mesophase appearing before the smectic A phase. A close