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Characterization of Thermal Decomposition Products of Cerium Acetate by High Temperature FTIR Spectroscopy

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Abstract

In the present work, thermal decomposition of cerium(III) acetate hydrate ($Ce(CH_3CO_2)_3 \cdot 1.5H_2O$) was studied in argon gas atmosphere by using thermogravimetric-differential thermal analysis techniques (TG-DTA) and *in-situ* High Temperature FTIR Spectroscopy technique (HT-FTIR). The obtained FTIR results were combined with the results of performed TG/DTA experiments in the present work and the literature data. A good agreement between the thermal analyses and FTIR results was found, and possible decomposition mechanism is discussed.

Keywords: HT-FTIR, Thermal decomposition, TG/DTA, Cerium(III) acetate hydrate

CHARAKTERYSTYKA PRODUKTÓW ROZKŁADU TERMICZNEGO OCTANU CERU ZA POMOCĄ WYSOKOTEMPERATUROWEJ SPEKTROSKOPII FTIR

W prezentowanej pracy, zbadano rozkład termiczny uwodnionego octanu ceru(III) ($Ce(CH_3CO_2)_3 \cdot 1,5H_2O$) w atmosferze argonu przy użyciu techniki termograwimetrycznej i termicznej analizy różnicowej (TG-DTA) oraz wysokotemperaturowej spektroskopii w podczerwieni *in-situ* z transformacją Furiera (HT-FTIR). Wyniki badań FTIR połączono z wynikami analizy TG/DTA i danymi literaturowymi. Stwierdzono dobrą zgodność pomiędzy wynikami analizy termicznej i FTIR oraz dyskusji poddano prawdopodobny mechanizm rozkładu.

Słowa kluczowe: HT-FTIR, rozkład termiczny, TG/DTA, uwodniony octan ceru(III)

1. Introduction

Ceria-based (DC) materials have recently been considered as the most promising solid electrolytes for intermediate temperature solid oxide fuel cell (IT-SOFC) applications, and been widely used for polishing and decolorizing glasses [1]. Thin film ceria has application areas in optical coatings and as a buffer layer for high-temperature superconductors. Doped and undoped ceria are usually prepared via thermal decomposition of its water soluble salts, especially, acetates. Since the properties of the obtained product directly influenced by the material and the decomposition products, it is crucial to understand the decomposition steps and intermediate products of cerium acetate. Numbers of experimental work have been reported using various *in-situ* and *ex-situ* techniques such as thermogravimetry with mass spectrometry (TG/DTA-MS) [2], X-ray diffraction with differential scanning calorimeter (XRD-DSC) [3]. However, the available literature data is limited and not reasonably in agreement. The present work aims to clarify inconsistencies in the literature by using *in-situ* high temperature infrared spectroscopy (HT-FTIR) technique. The obtained FTIR results were combined with the results of performed TG/DTA and DSC experiments in the present work and the literature data.

2. Experimental

Reagent grade cerium(III) acetate hydrate ($Ce(CH_3CO_2)_3 \cdot 1.5H_2O$) (Aldrich, 99.99 %), was used in the experiments. High Temperature Infrared Spectra (HT-FTIR) were recorded on Thermo-electron Nicolet FTIR-380 spectrometer under inert gas conditions using cerium(III) acetate hydrate (Aldrich) powder at 60, 180, 275 and 400°C as *in-situ* and *ex-situ*. The thermal decomposition behaviour of cerium(III) acetate hydrate was carried out by using thermogravimetric-differential thermal analysis (TG-DTA; Model Perkin Elmer Diamond) at a heating rate of 10 K/min under inert gas atmosphere using a flow rate of 100 ml/min. The TG/DTA experiments were conducted using platinum crucibles (sample mass: 30 mg) and α-Al_2O_3 powder was used as reference material for DTA.

3. Results and discussion

3.1. TG-DTA analyses

Fig. 1 shows the TG-DTA curves obtained using cerium(III) acetate hydrate at a constant heating rate of 10 K/min under argon flow. TG curve shows that the decomposition of $Ce(CH_3CO_2)_3 \cdot 1.5H_2O$ to cerium(IV) oxide reveals through several steps as it was reported in the literature [2-5]. The first wide strong endothermic peak observed in DTA curve indicated two endothermic reactions occurring at the same temperature interval due to the evaporation of moisture at around 105°C and the decomposition/dehydration of the crystal water. The observed weight loss was close to the theoretical value of 1.5 mole of crystal water. It can be given by following reaction:

$$Ce(CH_3CO_2)_3 \cdot 1.5H_2O \rightarrow Ce(CH_3CO_2)_3 + 1.5H_2O \quad (1)$$

Above dehydration, a relatively strong exothermic peak was observed in DTA curve at about 190°C (onset) with a peak temperature of 208°C. In the meantime, no weight change was determined in TG curve indicating a phase transition or crystallization reaction. As it was reported in the literature, the crystallization of amorphous cerium(III) anhydrous acetate, $Ce(CH_3CO_2)_3$, reaction takes places at about 200°C [2, 3]. The second endothermic peak represents a decomposition reaction. The peak temperature was determined at 281°C from DTA curve and a weight loss was observed in TG curve. The second endothermic reaction took place with a following third endothermic reaction representing two continuous reaction steps as given below:

$$8Ce(CH_3CO_2)_3 \rightarrow Ce_8O_3(CH_3CO_2)_{18} + 3(CH_3)_2CO + 3CO_2 \quad (2)$$

$$Ce_8O_3(CH_3CO_2)_{18} \rightarrow 8CeO(CH_3CO_2) + 5(CH_3)_2CO + 5CO_2 \quad (3)$$

With increasing temperature decomposition of organic components takes place resulting weak DTA signals and slight weight loss. The total weight loss at 750°C was about 50 %, which is in very good agreement with the theoretical value (49.98 %).

3.2. In-situ FTIR analyses

Fig. 2 shows FT-IR curves of cerium (III) acetate hydrate under inert (nitrogen) gas atmosphere between wave number of 4000–500 cm^{-1}. As can be clearly seen at lower temperatures the structure of cerium acetate does not change significantly. However, with increasing temperature the broad water peaks (at around 3600–3100 cm^{-1}) start to disappear, these peaks are considered as not only crystal water but also moisture. Similarly, with increasing temperature the intensity of the peaks (1624 cm^{-1}) dealing with the carbon oxygen bonds (C-O) decreases, which means organic content of the samples decrease significantly. The peak, showing the C-O single bond occurring around 1040 cm^{-1} also disappears with increasing temperature [5]. Above 400°C almost all of the organic related peaks disappeared, however, very small indications of the carbon peak (single and/or double bonds) can be seen. This situation is parallel to the TGA results showing slight decrease even above 600°C.

Ex-situ FTIR results are given in Fig. 3. The samples were heat treated under argon atmosphere at various temperatures and then air quenched under continuous argon flow. The obtained *in-situ* and *ex-situ* FTIR results are in quite good agreement with each other and with the literature [4, 5]. As can be clearly seen from the figure, at low temperatures, the intensities of the ceria peaks (700-350 cm^{-1}) are relatively low, showing the small amount of the transformed ceria. With increasing temperature, the organic related peaks such as symmetric stretching peaks of CO_3^{2-} (around 945 cm^{-1} of wave number) gradually decrease [5]. On the other hand, the ceria peaks increase drastically with increasing temperature, which is also in very good agreement with our *in-situ* results.

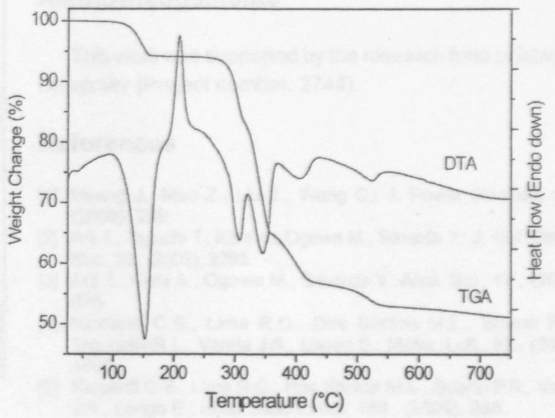

Fig. 1. TG-DTA curves of cerium (III) acetate hydrate under under argon atmosphere at 10 K/min heating rate.

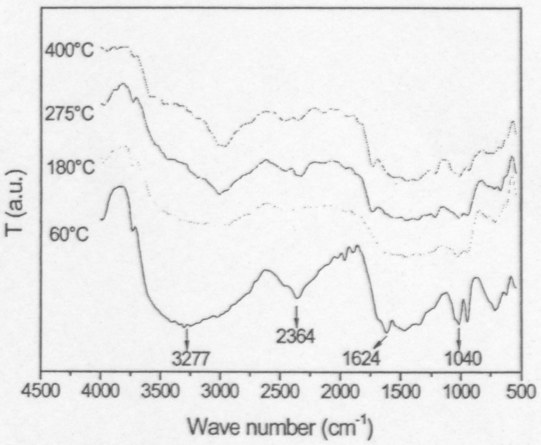

Fig. 2. In-situ FTIR spectra of cerium (III) acetate hydrate under nitrogen gas atmosphere.

4. Conclusions

The thermal decomposition of $Ce(CH_3CO_2)_3 \cdot 1.5\ H_2O$ to cerium(IV) oxide in inert gas atmosphere takes place in various decomposition steps including exothermic and endothermic reactions.

TG and DTA results pointed out that the thermal decomposition reactions completed at around 600°C. However even above 600°C small carbon peak were determined in the FTIR results indicating residual carbon.

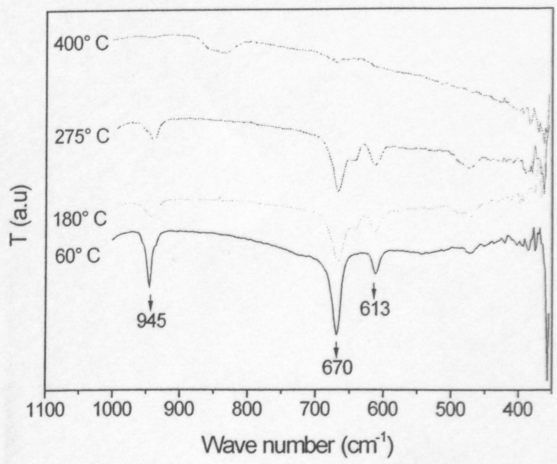

Fig. 3. Ex-situ FTIR spectra of the samples heat treated at the given temperatures.

In-situ FTIR results show that cerium(III) acetate hydrate is stable up to 60°C, above 100°C water and carbon groups start to disappear. All of the water peaks completely disappeared at ~400°C, but small carbon peaks still appear, which is in agreement with the DTA results. These results were confirmed with the *ex-situ* FTIR results. The results also show that cerium acetate hydrate starts to decompose above 100°C, and in various exothermic and endothermic steps, and ceria (CeO_2) forms above 400°C having a small amount of residual carbon.

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