



Investigation of Thermal Decomposition Behavior of Cerium (III) Acetate Hydrate in Argon and Dry Air Atmosphere

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ABSTRACT

The thermal decomposition behavior of Cerium (III) Acetate Hydrate, $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$, was investigated by using *in-situ* High Temperature FTIR Spectroscopy (in N_2), High Temperature X-ray diffraction (HT-XRD) (in air) and TG/DTA - MS techniques (Ar and dry air). Thermal decomposition of $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$ to CeO_2 , ceria, in argon occurred through several endothermic and exothermic reactions. Through these consecutive reactions, amorphous cerium anhydrous acetate formed above the dehydration temperature. Afterwards, crystallization of the anhydrous acetate took place with the increasing temperature and ceria formed in cubic phase as the final product. In dry air, the decomposition reaction is completed around 330°C and CeO_2 was formed as the final product. The difference between the two atmospheres was significant in between 250 - 550°C . The activation energy for the crystallization of cerium anhydrous acetate was determined as 244 kJ mol^{-1} under non-isothermal conditions by using Kissinger equation.

Keywords: $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$, Ceria, HT-XRD, Thermal decomposition

1. INTRODUCTION

Doped ceria-based materials have recently been considered as the most promising electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC) [1-3]. They also find use in structural and electronic promoters for heterogeneous catalytic reactions and polishing and decolorizing agents in glasses [4, 5]. Additionally, thin film ceria has been used in optical coatings and in high-temperature superconductors as a buffer layer [6, 7]. Ceria based materials are usually prepared via thermal decomposition of their water soluble salts; especially from their acetates. Decomposition of $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$ to cerium (IV) oxide, ceria, takes place through a series of endothermic and exothermic reactions. Since the properties of the obtained product is directly influenced by the starting material and the

decomposition products, it is crucial to understand the decomposition steps and the intermediate products of cerium acetate. In recent experimental works [8-10], the decomposition mechanism of cerium acetate hydrate was investigated by using *in-situ* and *ex-situ* techniques, such as thermogravimetry combined with mass spectroscopy (TG/DTA-MS), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). It was reported that the formation of the amorphous cerium (III) anhydrous acetate $\text{Ce}(\text{CH}_3\text{CO}_2)_3$ realized above the dehydration temperature [8-10]. The decomposition reactions are dependent on the thermal history and the process variables. In this study, argon and dry air atmospheres were used to investigate the behavior of Cerium (III) Acetate Hydrate by a thermal analysis technique. The difference between the two atmospheres was significant

in between 250-550°C. In dry air, the reaction is completed around 330°C and CeO₂ is formed as the final product. Whereas in argon atmosphere, series of endothermic peaks were observed and there decomposition intermediate products were formed to be Ce₈O₃(CH₃CO₂)₁₈, 8CeO(CH₃CO₂) and Ce₂O₂CO₃. In addition, high temperature FTIR in nitrogen was carried out to characterize the structure at bond types. There is no data in literature about activation energy values for the crystallization of cerium (III) anhydrous acetate, activation energy of the crystallization of cerium (III) anhydrous acetate was determined under non-isothermal conditions by using Kissinger method.

2. EXPERIMENTAL

In the experimental studies, reagent grade cerium (III) acetate hydrate (Ce(CH₃CO₂)₃·1.5H₂O) (Aldrich, 99.99 %) was used. High temperature infrared spectra were recorded using Perkin Elmer (Spectrum 100) FTIR spectrometer with high temperature diffuse reflectance attachment from Pike (DiffuseIR). The FTIR resolution was 4.0 cm⁻¹, and the scanned wave number range was selected between 4000 and 350 cm⁻¹. *In-situ* FTIR experiments were carried out under nitrogen gas flow (flow rate of 100 ml.min⁻¹) at a heating rate of 5 K min⁻¹ from room temperature to 650 °C.

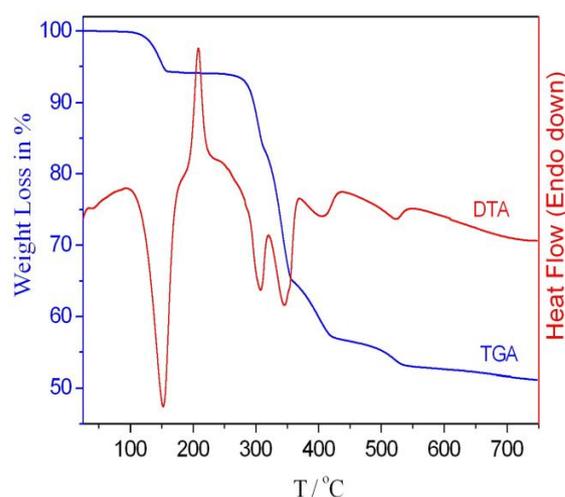
The thermal decomposition of the cerium (III) acetate hydrate was investigated by using thermogravimetric-differential thermal analysis technique (TG-DTA: TA, SDT-Q600) up to 750 °C, with a heating rate of 5 K min⁻¹ in argon and dry air atmosphere (flow rate of 100 ml.min⁻¹). A mass spectrometer (MS: Pfeifer, ThermoStar, GSD301T3) was attached to the TG/DTA setup in order to analyze the product gases simultaneously. TG-DTA experiments were carried out in alumina crucibles (sample mass: ~30 mg) and α-Al₂O₃ powder was used as the reference material. Differential scanning calorimeter (DSC: Netzsch, Phoenix DSC204-F1) was used for the kinetic studies. The DSC experiments were performed in aluminum pans under argon atmosphere (flow rate of 25 ml min⁻¹) with different heating rates (5, 10, 15, 20 K min⁻¹). The residual carbon contents of the samples were determined by applying hot extraction technique (Eltra GmbH, C-S 2000). High temperature X-ray diffraction method was used for phase characterization in air using Rigaku DMax / 2200 PC diffractometer with CuKα radiation (λ=1.54056 Å).

3. RESULTS AND DISCUSSION

3.1. Thermal Analysis

Figure 1 shows the TG-DTA curves of cerium (III) acetate hydrate under argon flow. The TG-DTA curves show that the decomposition of Ce(CH₃CO₂)₃·1.5 H₂O to ceria took place through several endothermic and exothermic reactions which was also reported in the literature [8, 9]. 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 the moisture at around 110°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. As it can be clearly seen from MS data in Figure 2, the gases evolved during the dehydration reaction of crystal water and moisture were identified as water vapor (main ions of m/z: 17, 18 assigned to OH, H₂O, respectively). After dehydration, a relatively strong exothermic peak was observed in DTA curve (see Figure 1) at about 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(CH₃CO₂)₃, reaction takes place at about 200°C [9,10]. Consistent with the literature data, no gas release was detected by MS data (see Figure 2), proving a crystallization or phase transition reaction at around 208 °C which was also observed in TG curve. The second endothermic peak represents a decomposition



reaction.

Figure 1. TG-DTA curves of cerium (III) acetate hydrate under Argon atmosphere.

The peak temperature was determined at 307°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. The first step started at peak temperature at 307 °C as determined by both MS (Figure 2) and TG curves (Figure 1). In the second step (third endothermic peak) a stronger peak was observed at 338°C in DTA curve with a higher weight loss in TG curve. The MS curves (see Figure 2) clearly show that the reaction products obtained were carbon monoxide (m/z: 28), carbon dioxide (m/z: 44) and acetone (m/z: 15, CH₃⁺; m/z: 43, CH₃CO⁺, and m/z: 58, (CH₃)₂CO⁺) at the temperature range of 307 and 338°C.

According to the proposed reactions by Arii et al [9,10], which was also presented by Mayer and Kassiere for rare-earth acetates [8], the possible decomposition reaction step, which was also determined in MS data from the observed second and third endothermic peaks in DTA was given as follows:

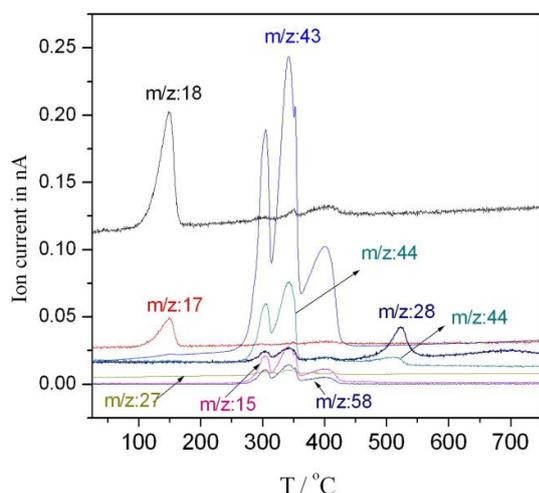
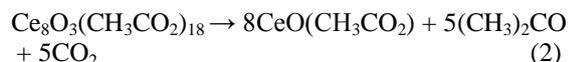
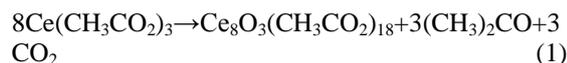


Figure 2. MS curves of cerium (III) acetate hydrate under Argon atmosphere.

The fourth endothermic peak in DTA curve (peak temperature of 406°C) represents a decomposition reaction releasing acetone as a product which was determined by MS curve in Figure 2. The weight loss determined from TG curve according to this step was about 8 % which is in good agreement with calculated literature data [9,10]. The possible reaction was given as:



The last endothermic peak was determined with the peak temperature of 523 °C. As it can be seen from the MS results (Figure 2), the reaction products of the last endothermic reaction were found to be CO as it was expected from the given reaction (4). Apart from CO release, very low amount of CO₂ was also observed in MS data for this reaction step. Above this temperature, a slight weight loss was determined in TG curve at about 700 °C indicating the release of CO which was observed from MS curves. The results were in agreement with the literature, showing the decomposition of ceriumoxycarbonate and release of CO₂ and CO gas.

The TG-DTA curves of the experiments carried out under dry air conditions are given in Figure 3. Although the first two steps of the reactions are the same for the samples investigated under argon and dry air conditions, at higher temperatures a complete different behavior was observed under dry air atmosphere. The first endothermic peak observed in DTA curve was due to the evaporation of moisture and dehydration of crystal water with a weight loss observed in TG curve. The second small exothermic peak (at about a peak temperature of 208°C) indicated the crystallization of amorphous cerium (III)

anhydrous acetate which is the same for the experiments realized under argon atmosphere. The peak temperatures determined for these endothermic (first step of decomposition reaction in dry air) and exothermic reactions were found to be similar to the sample investigated under argon atmosphere. On the other hand, above the temperatures of 250°C, only one strong exothermic peak was observed in DTA curve with a large weight loss in TG curve (see Figure 3).

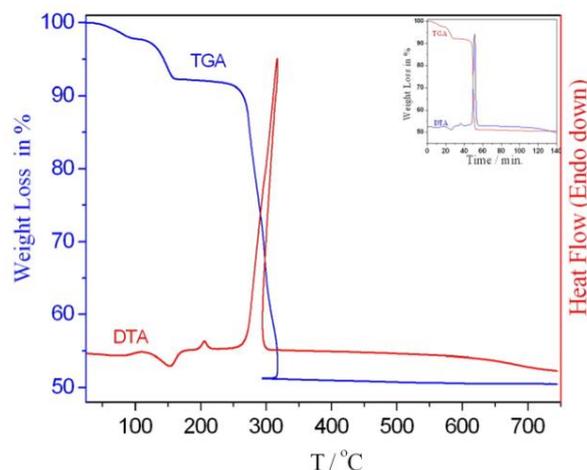


Figure 3. TG-DTA curves of cerium (III) acetate hydrate under dry air atmosphere. Inset shows the TG/DTA change versus time

This strong exothermic peak is due to the combustion reaction of organic materials under dry air atmosphere (e.g. burn out of acetone) took place in a single step. At the same time acetate is decomposed which is clearly in Figure 4. That results in (m/z: 15, CH₃⁺; m/z: 43, CH₃CO⁺). Possible reactions in dry atmosphere are as follows:

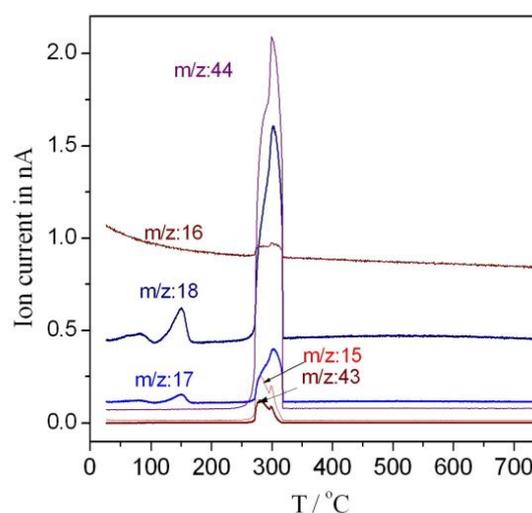


Figure 4. Mass spectra of cerium (III) acetate hydrate under dry air atmosphere.

Figure 4 shows the mass spectra of cerium (III) acetate hydrate under dry air atmosphere. The MS data in Figure 4 confirmed that H_2O (m/z : 17, 18) was the main product released for the first endothermic peak. For the second exothermic peak observed in DTA, the main gases released determined from MS data were a mixture of carbon dioxide (m/z : 44) and acetone (m/z : 15, 43). Due to the strong nature of the exothermic reaction occurred by the burning of the organic materials with the air atmosphere a large weight loss was observed in TG curve. Above 400°C , no weight loss or a change in MS signal was recorded showing steady behavior.

3.2. In-situ High Temperature XRD Characterization

High temperature X-ray diffraction (XRD) patterns obtained under dry air condition are given in Figure 5. The XRD patterns obtained at 60 and 110°C , which represents the dehydration temperature range, showed the presence of cerium acetate hydrate (PDF 22-0162). However, the pattern obtained at 180°C showed an amorphous structure with a few broad peaks revealing the beginning of the crystallization of ceria which is in good agreement with the literature results [9,10]. The XRD results were also supported with the TG-DTA analyses showing an exothermic crystallization reaction without any weight loss from amorphous anhydrous acetate above this temperature range (see Figure 3 the first exothermic peak).

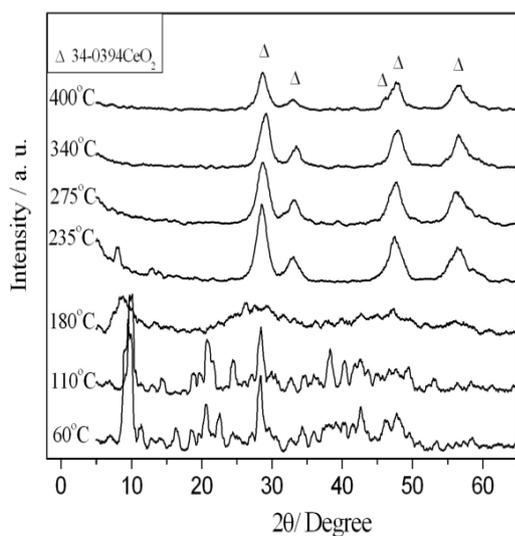


Figure 5. In-situ High Temperature XRD patterns obtained at temperatures between 60°C and 400°C .

As can be seen from the patterns in Figure 5, CeO_2 started to form at around 180°C and the peak intensities of CeO_2 increased with the increasing temperature, indicating the crystallization of CeO_2 with cubic (fluorite) crystal structure was completed at a final temperature of 400°C .

3.3. In-situ High Temperature FTIR

The results obtained from *in-situ* HT-FTIR experiments are given in Figure 6. The strong intense bands observed at 27°C were found to be in the range of $3000\text{--}3700\text{ cm}^{-1}$, at 1536 , 1415 , 1019 , 940 cm^{-1} and below 700 cm^{-1} .

The two weak bands detected in the wave number of $2935\text{--}2857\text{ cm}^{-1}$ were assigned to $\text{C}\text{--}\text{CH}_3$ asymmetric stretching vibrations. The bands at 1019 cm^{-1} and 940 cm^{-1} were assigned to symmetric stretching of $\text{C}\text{--}\text{O}$, CO_3^{2-} , respectively. The intense bands detected in the range of $3000\text{--}3700\text{ cm}^{-1}$ and at 1536 cm^{-1} are attributed to $\text{O}\text{--}\text{H}$ stretching of physically absorbed H_2O or surface --OH group. The band at around 1415 cm^{-1} corresponds to CO asymmetric vibration [11-13]. By increasing the temperature, at 220°C the hydroxyl groups of absorbed water were disappeared significantly. However, the intensity of the bands at 1415 , 2935 and 2857 cm^{-1} decreased with the increasing temperature. When the temperature reached to 640°C , the bands of CO group almost disappeared. At 640°C , the low intensity bands in the range of 400 and 700 cm^{-1} are attributed to the $\text{Ce}\text{--}\text{O}$ stretching vibrations, indicating the structural transformation of cerium (III) acetate hydrate to CeO_2 [11,12,14].

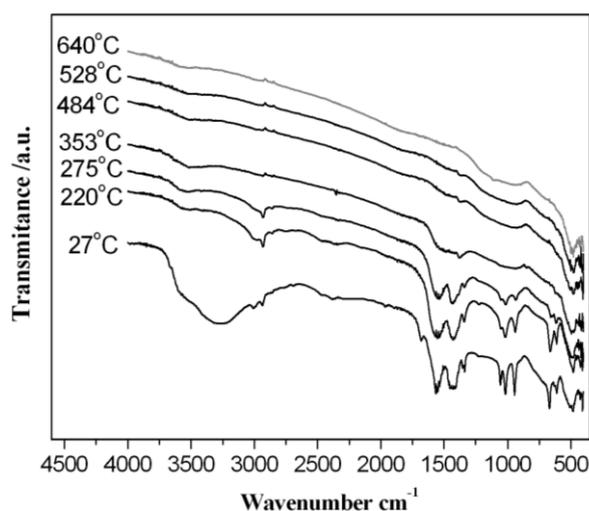


Figure 6. High Temperature FTIR curves of cerium (III) acetate hydrate under nitrogen gas atmosphere.

According to the results obtained from TG/DTA, MS and HT-FTIR experiments realized under inert gas atmosphere, it was concluded that with increasing temperature low amount of residual carbon were present in the system. In order to determine the residual carbon content of the samples, hot extraction method was used. It is clearly seen from Figure 7 that the increase in heat treatment temperature resulted in sharp decrease on the residual carbon content. However, even the sample heat treated at 800°C , small amount of carbon content (about 0.1%) was observed.

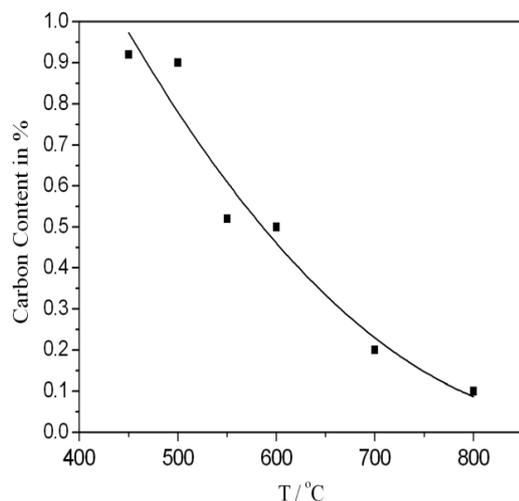


Figure 7. Residual carbon content vs temperature of heat treated cerium (III) acetate

3.4. Crystallization Kinetics of Anhydrous Acetate

The crystallization kinetics of the anhydrous acetate was investigated under non-isothermal experimental conditions by using differential scanning calorimeter (DSC). Continuous heating curves of the cerium (III) acetate hydrate at various heating rates are shown in Figure 8. The first endothermic peaks in Figure 8 represent the dehydration reaction. The second exothermic peak is attributed to the crystallization reaction of the anhydrous acetate. Crystallization kinetic experiments were realized for the second exothermic peaks.

According to the Kissinger equation [15] which is given below:

$$\ln(T_p^2/\beta) = E/RT_p + \text{constant} \quad (6)$$

E : Activation energy (J mol^{-1})

T_p : peak temperature (K)

β : Heating rate (K min^{-1})

R : gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$)

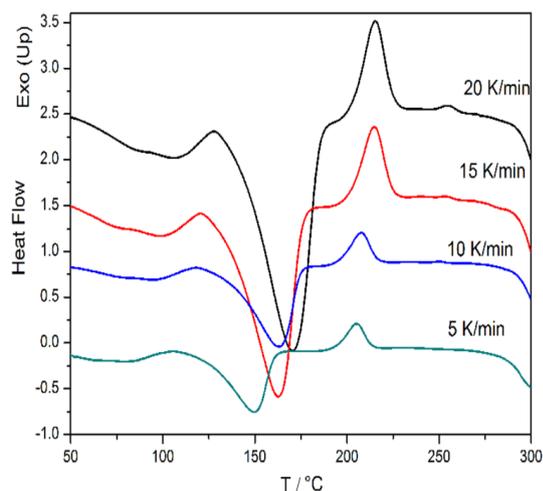


Figure 8. DSC curves of cerium (III) acetate hydrate with different heating rates under argon atmosphere.

By using equation 6 the activation energy of the crystallization reaction (E) can be determined using Kissinger method with DSC scans recorded at different heating rates. In the present study four different heating rates were selected ($5, 10, 15, 20 \text{ K min}^{-1}$) for the DSC experiments. With increasing heating rate the peak temperatures shifted to higher temperature values. The peak temperatures (T_p) determined from Figure 8 for the crystallization of anhydrous acetate phase were found to be $205, 210, 213, 216 \text{ }^\circ\text{C}$ for heating rates of $5, 10, 15, 20 \text{ K min}^{-1}$, respectively.

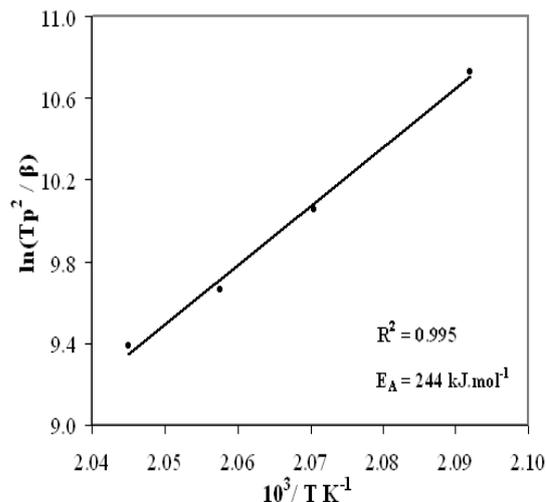


Figure 9. Kissinger plot for the determination of the activation energy.

By using the values of peak temperatures, a plot of $\ln(T_p^2/\beta)$ vs $1/T_p$ yields approximately straight line as shown in Figure 9. From the slope of this line the activation energy of the crystallization of anhydrous acetate was determined. The activation energy value (E) was calculated as 244 kJ mol^{-1} . There is no experimental data in the literature on the crystallization of amorphous anhydrous cerium acetate. Therefore, the first experimental data was recorded for the crystallization reaction of the anhydrous acetate.

4. CONCLUSION

The thermal decomposition of $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot 1.5\text{H}_2\text{O}$ to cerium (IV) oxide (ceria) was investigated in argon and dry air atmospheres. The experiments realized in argon atmosphere took place in various decomposition steps with several exothermic and endothermic reactions. TG-DTA results pointed out that the thermal decomposition reactions completed in argon atmosphere at around $600 \text{ }^\circ\text{C}$. The experiments conducted under dry air conditions showed a complete different behavior than the argon atmosphere. A strong exothermic reaction following a weak endothermic and an exothermic reaction related to the burn out of the organic materials (acetone like) was observed in dry air. In both atmosphere conditions CeO_2 was obtained as the final product. Amorphous anhydrous acetate was obtained as the dehydration reaction product of cerium acetate hydrate. Crystallization of the amorphous anhydrous acetate phase started around $180 \text{ }^\circ\text{C}$, which was confirmed with TG-DTA and HT-

XRD analyses. HT-FTIR analyses were performed for the first time to investigate the change in bond structure during the formation of cerium (III) acetate hydrate to ceria. The crystallization behavior of anhydrous acetate was investigated applying DSC experiments under non-isothermal conditions up to 300°C. The activation energy of the crystallization of amorphous anhydrous cerium acetate was determined for the first time by using Kissinger equation. The activation energy was found to be 244 kJ mol⁻¹.

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REFERENCES

- [1] Steele, B.C.H., Appraisal of Ce_{1-y}Gd_yO_{2-y/2} electrolytes for IT-SOFC operation at 500 °C, *Solid State Ionics*, 29 : 95-110, (2000).
- [2] Inaba, H. and Tagawa, H., Ceria-based solid electrolytes – Review, *Solid State Ionics*, 83: 1-16, (1996).
- [3] Solak, N., Zinkevich, M., Aldinger, F. et al., Reactivity in the systems LaGaO₃/Ni and CeO₂/Ni, *Fuel Cells*, 2 : 87-92,(2006).
- [4] Trovarelli, A., Catalytic properties of ceria and CeO₂-containing materials, *Catal. Rev.-Sci. Eng.*, 38 : 439-520,(1996).
- [5] Yao, H.C. and Yao, Y.F.Y., Ceria in automotive exhaust catalysts I. Oxygen storage, *J. Catal.*, 86: 254-265, (1984).
- [6] Ozer, N., Optical properties and electrochromic characterization of sol-gel deposited ceria films, *Solar Energy Materials and Solar Cells*, 68: 391-400, (2001).
- [7] Wu, X.D., Dye, R.C., Muenchausen, R.E., Foltyn, S.E., Maley, M., Rollett, A.D., Garcia, A.R., Nogar, N.S., Epitaxial CeO₂ Films as Buffer Layers for High-Temperature Superconducting Thin-Films, *Appl. Phys. Lett.* 58 : 2165-2167, (1991).
- [8] Mayer, I. and Kassiere, F., A thermogravimetric study of the lighter rare earth acetates, *J Inorg. Nucl. Chem.*, 28: 2430-2432, (1966).
- [9] Arii, T., Taguchi, T., Kishi, A., Ogawa, M., Sawada, Y. et al., Thermal Decomposition of Cerium (III) Acetate Studied with Sample-controlled Thermogravimetric-mass Spectrometry (SCTG-MS), *J. Eur. Ceram. Soc.*, 22: 2283-2289, (2002).
- [10] Arii, T., Kishi, A., Ogawa, M., Sawada, Y. et al., Thermal Decomposition of Cerium (III) Acetate Hydrate by a Three-dimensional Thermal Analysis, *The Jpn. Soc. For Anal. Chem.*, 17: 875-880, (2001).
- [9] Dos Santos, M.L., Lima, R.C., Riccardi, C.S., Tranquilin, R.L., Bueno, P.R., Varela, J.A., Longo, E. et al., Preparation and characterization of Ceria Nanospheres by Microwave-hydrothermal Method, *Mater. Lett.*, 62: 4509-4511,(2008) .
- [12] Riccardi, C.S., Lima, R.C., Dos Santos, M.L., Bueno, P.R., Varela, J.A., Longo, E., *Solid State Ionics*, 180: 288-293, (2009).
- [13] Nakanishi, K., Solomon, P. H., *Infrared Absorption Spectroscopy*, 2 nd ed., Holden-Day ,Inc., San Francisco, (1977).
- [14] A. Brăileanu, S. Mihaiu, M. Bán, J. Madarász and Pokol, *Thermoanalytical Investigation Tin and Cerium Salt Mixures*, *J. Therm. Anal. Cal.*, 80: 613-618, (2005).
- [15] Kissinger, H., *Reaction Kinetics in Differential Thermal Analysis*, *Anal. Chem.*, 29: 1702-1706, (1957).