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# THERMAL DECOMPOSITION OF AMMONIUM CEROUS CARBONATE

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The thermal decomposition of ammonium ceryl(III) carbonate (ACeC) [$NH_4CeO(CO_3)$] was investigated by thermogravimetry, differential thermal analysis and X-ray diffraction.

The results showed three endothermic stages of decomposition, each involving a loss in weight. The first stage, at 65.5 °C, is characteristic of the removal of adsorbed water, the second stage, at 214.8 °C, is associated with ammonia release, and the third stage, at 263.6 °C, relates to the removal of carbon dioxide.

Ceria ($CeO_2$) is considered a good refactory material, since it has a high melting point (2600°). Ceria is analogous in its behaviour to plutonia ($PuO_2$). The preparation and characteristics of ceria are therefore of great interest from a nuclear point of view. It can be considered for high-temperature fuel cell applications [1, 2]. Electroconductive ceramic materials containing $CeO_2$ are suggested for the increase of thermal stability.

The aim of this study was to investigate the thermal decomposition behaviour of ammonium ceryl(III) carbonate (ACeC) by means of TG, DTA and X-ray diffraction.

## Experimental

ACeC powders were prepared by using an established technique [3]. The conditions of precipitation were as follows:

| | Temp., °C | pH | C/Ce |
|---|---|---|---|
| Powder A | 40 | 8.3 | 2 |
| Powder B | 40 | 8.6 | 2 |

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Precipitating agent for powder A: 25% $NH_4HCO_3$ mixed with 10% $NH_4OH$. For powder B: 25% $NH_4HCO_3$ with prior addition of 10% $NH_4OH$.

The experiments in this work were carried out on a DuPont thermal analyser (type 1090), in static air, in the temperature range 25–950°, at a heating rate of 10 deg/min.

X-ray investigation of the ACeC and $CeO_2$ powders was performed with a Philips diffractometer (type 1140). The patterns were run with Cu as target and Ni as filter ($\lambda = 1.54178$ Å), at 40 kV and 30 mA, with a scanning speed of 2 deg/min.

## Results and discussion

The precipitated ACeC powders were yellow. Figure 1 shows a typical DTA curve for the decomposition of ACeC powder of type A to $CeO_2$ in static air at a heating rate of 10 deg/min. Figures 2 and 3 depict the TG curves for the decompositions of ACeC powders of types A and B, respectively.

The thermal analysis results reveal three stages of decomposition, each involving a loss in weight. The three stages of TG are listed in Table 1, together with the peak temperatures.

The TG and DTA curves indicate that the three stages are endothermic. The first stage is characteristic of the removal of adsorbed water, the second of the removal of ammonia, and the third of carbon dioxide release. The peaks are maximized at 65.5, 214.8 and 263.6° for powder A, and at 38.5, 192.5 and 224.1° for powder B.

The results in Table 1 indicate that the removal of $NH_3$ and $CO_2$ occurred at lower temperatures for powder B than for powder A. This could be due to the high specific surface area of powder B, as determined by the BET method. For type A the area was 2.81 $m^2/g$, whereas for type B it was 7.42 $m^2/g$.

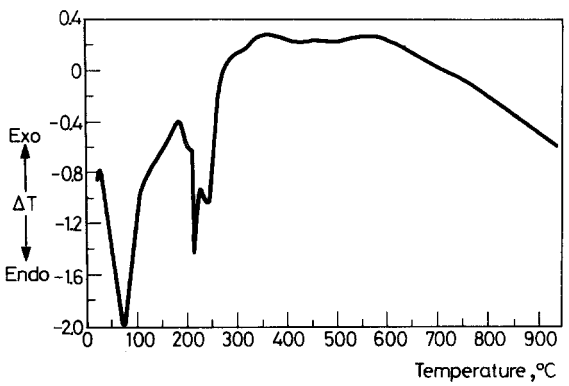


**Fig. 1 DTA curve of ACeC powders of type A**

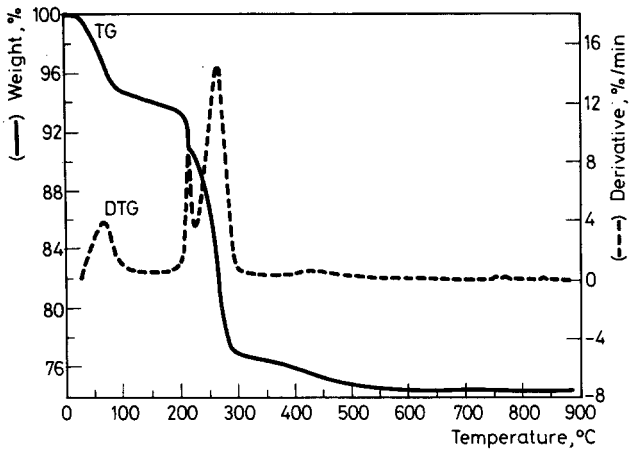


**Fig. 2** TG and DTG curves of ACeC powders of type A

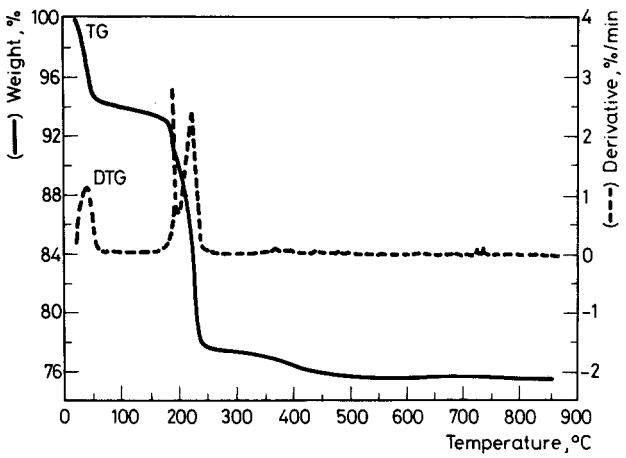


**Fig. 3** TG and DTG curves of ACeC powders of type B

**Table 1** DTA of ACeC powders of types A and B at heating rate of 10 deg/min

| Stage | Peak temperature, °C | | Type of deflection | Function |
|---|---|---|---|---|
| | Type A | Type B | | |
| I | 65.5 | 38.5 | endothermic | removal of adsorbed water |
| II | 214.8 | 192.5 | endothermic | $NH_3$ release |
| III | 263.6 | 224.1 | endothermic | $CO_2$ release |

The TG and DTG curves reveal total weight losses of 23.26 and 22.4% for powders of types A and B, respectively. These values are close to the theoretical weight loss (26.49%) calculated from the decomposition equation for ACeC. Table 2 shows the various stages of weight losses within the different temperature ranges.

**Table 2** TG of ACeC powders of types A and B at heating rate of 10 deg/min

| Stage | Temp. range, °C | Weight loss, % | | Function |
|---|---|---|---|---|
| | | Type A | Type B | |
| I | 25–180 | 5.81 | 6.26 | removal of adsorbed and crystalline water |
| II | 180–210 | 3.88 | 3.83 | removal of $NH_3$ gas |
| III | 210–260 | 13.57 | 12.41 | removal of $CO_2$ gaas |

*X-ray diffraction analysis*

The X-ray diffraction data on the obtained ACeC powders were compared with those on the cerium oxycarbonate prepared by Bentzen et al. [4]. Table 3 gives the lattice parameters ($d$) and relative intensities ($I/I_0$) of our powders and those reported by Bentzen et al. for a powder prepared by hydrolysis. A comparison demonstrates that our powder has a similar structure to that of the cerium oxycarbonate.

**Table 3** X-ray diffraction data on ACeC powder compared with those of Bentzen et al. [4]

| $d$, Å | | $I/I_0$ | |
|---|---|---|---|
| This work | Bentzen et al. [4] | This work | Bentzen et al. [4] |
| — | 6.417 | — | 6.8 |
| 5.556 | 5.574 | 32.0 | 30.3 |
| 4.320 | 4.311 | 100.0 | 100.0 |
| 3.717 | 3.723 | 65.0 | 60.0 |
| 3.359 | 3.363 | 46.0 | 43.6 |
| 2.954 | 2.959 | 75.0 | 77.0 |
| 2.658 | 2.659 | 34.0 | 36.2 |
| 2.507 | 2.508 | 33.0 | 39.0 |
| 2.432 | 2.429 | 23.0 | 26.1 |
| 2.347 | 2.347 | 80.0 | 79.5 |

The X-ray diffraction data on the $CeO_2$ powders of types A and B are in good agreement with the data on ASTM 4–0593 Card, as shown in Table 4.

**Table 4** X-ray diffraction data on $CeO_2$ powders compared with the standard ASTM 4–0593 Card data

| This work | | | | ASTM 4–0593 | |
|---|---|---|---|---|---|
| Powder A | | Powder B | | | |
| $d$, Å | $I/I_0$ | $d$, Å | $I/I_0$ | $d$, Å | $I/I_0$ |
| 3.1237 | 100 | 3.1326 | 100 | 3.124 | 100 |
| 2.7045 | 35.46 | 2.7089 | 37.72 | 2.706 | 29 |
| 1.9135 | 71.98 | 1.9149 | 63.014 | 1.913 | 51 |
| 1.632 | 57.75 | 1.6337 | 57.35 | 1.632 | 44 |
| 1.5628 | 9.41 | 1.5634 | 9.77 | 1.562 | 5 |
| 1.3536 | 12.173 | 1.3534 | 10.776 | 1.353 | 5 |

## Conclusions

The thermal decomposition of ammonium ceryl(III) carbonate occurs in three endothermic stages, each involving a loss in weight. The first stage involves the removal of adsorbed and crystalline water, the second stage ammonia release and the third stage the removal of carbon dioxide. The stages of ammonia and carbon dioxide loss are affected by the specific surface area of the powder. The loss of $NH_3$ and $CO_2$ occurred at lower temperatures from powder B than from powder A. This could be to the high specific surface area of powder B.

The total weight losses of 23.26 and 22.4% for powders A and B, respectively, are close to the theoretical weight loss (26.49%) for ACeC decomposition.

## References

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3 N. Abdelmonem and A. S. Abdel-Halim, A Developed Technique for Ceria Pellet Fabrication, submitted for publication to J. Chem. Tech. Biotech., 1987.

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**Zusammenfassung** — Mittels Thermogravimetrie, Differentialthermoanalyse und röntgendiffraktion wurde die thermische Zersetzung von Ammonium-zer(III)-karbonat (ACeK) $[NH_4CeO(CO_3)]$ untersucht. Die Ergebnisse zeigen drei jeweils mit Gewichtsverlust verbundene endotherme Zersetzungsschritte. Während des ersten Schrittes wird bei 65.5 °C adsorbiertes Wasser, anschließend im zweiten Schritt bei 214.8 °C Ammoniak und letztendlich im dritten Schritt bei 263.6 °C Kohlendioxid abgegeben.

**Резюме** — Методом термогравиметрии, дифференциального термического анализа и рентгенофазового анализа изучено термическое разложение аммониевой соли карбоната трехвалентного цеуия $[NH_4CeO(CO_3)]$. Результаты показали три эндотермические стадии разложения, сопровождающиеся потерей веса. На первой стадии при температуре 65,5 °C происходит выделение адсорбированной воды, на второй — при температуре 214,8 °C рьоисходит выделение аммиака, а на третьей стадии при температуре 263,6 °C — выделение двуокиси углерода.