Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 3, 939–944

MECHANISM OF THERMAL DECOMPOSITION OF ZIRCONYL OXALATE $ZrOC_2O_4$

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Thermal decomposition of zirconyl oxalate hydrate was studied using DTA, TG, QMS and XRD techniques. It was shown that decomposition occurs in two stages: dehydration to anhydrous oxalate and next, decomposition to zircon oxide (zirconia). These steps are not well separated. We observed that significant amount of water are released during second stage of decomposition. Zircon dioxide is obtained in tetragonal form. Moreover, we consider some dependences between conditions of preparations zirconyl oxalate hydrate and some properties of solid product of its decomposition.

Although the reaction of thermal decomposition of zirconyl salts is generally utilized in technology, many aspects of this process are still not sufficiently explained. In our work, we present some new interesting observations concerning thermal behaviour of zirconyl oxalate.

Keywords: *microstructure, thermal decomposition, zirconyl oxalate*

Introduction

Zirconyl oxalate is technologically important material which can be used as a precursor for the preparation of either pure zircon dioxide (zirconia) or zirconia mixed with other oxides. The main interest for investigation of zirconia results from its chemical stability, as well as specific electrical and catalytical properties. Nanocrystalline zirconia is extensively examined as a material for inorganic membranes and as a catalyst support. For example, Liu *et al.* [1] successfully tested zirconia as a catalyst in the process of methanol synthesis. The wide application of zirconia is also due to the possibility of its physical properties, surface and pore structure modification by controlling of synthesis conditions. In case of applying zirconyl oxalate as a precursor for zirconia, two ways of synthesis of $ZrOC_2O_4$ are used. The first one is precipitation of oxalate by mixing solutions of oxalic acid and zirconyl salt (the most often used salt is $ZrOCl_2 \cdot 8H_2O$) [2–4]. The second method is based on hydrolysis of double zirconyl salts (for example sodium zirconyl oxalate $Na_2ZrO(C_2O_4)_2$ [5]). The appropriate value of pH during precipitation is the most important condition which must be retained. Otherwise, hydrated zircon oxide would precipitate simultaneously with zirconyl oxalate hydrate.

The mechanism of thermal decomposition of zirconyl oxalate hydrate was considered in a few papers [4, 5, 7] but there are many discrepancies in presented results. In all the papers decomposition is described as a two-stage process: dehydration and partially (or completely) dehydrated salt decomposition. These two stages cannot be clearly separated. According to Etienne [4] and Ju [7], when decomposition is carried out in air, the first endothermic stage of dehydration leads to anhydrous salt:

$$ZrO(C_2O_4)\cdot 3H_2O \xrightarrow{\approx 432\ K} ZrO(C_2O_4)+3H_2O$$

Next, at about 608 K anhydrous zirconyl oxalate in endothermic stage decomposes to amorphous zirconium dioxide:

$$ZrO(C_2O_4) \xrightarrow{608-613\ K} ZrO_2+CO_2+CO$$

Continuation of heating leads to crystallization of amorphous zirconia to tetragonal crystallographic form, at the temperature ca. 743 K. This crystallization was not observed by Agarwal and Naik [8]. Tetragonal form of ZrO_2 transforms to monoclinic at 1043 K, which is accompanied by the exothermic effect.

Some unexpected agreement (especially concerning number of moles of water per mole of $ZrOC_2O_4$) between results reported by Etienne and Ju is observed, although ways of preparation of the samples before TG/DTA experiment, as well as heating rates were different. It was also mentioned by Etienne [4] that releasing of hydrogen chloride takes place during the whole thermal treatment. The rate of HCl release increased during crystallization and phase transformation.

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1388–6150/$20.00

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Sharma *et al.* in the survey of literature data [5] proposed the following scheme of thermal decomposition of $ZrOC_2O_4$ in air (based on Gangadevi *et al.* work [9]):

$$ZrO(C_2O_4)\cdot 5.5\ H_2O \xrightarrow{298-473\ K} ZrO(C_2O_4)\cdot 1.5H_2O+4H_2O$$

$$ZrO(C_2O_4)\cdot 1.5\ H_2O \xrightarrow{473-673\ K} ZrO_2+1.5\ H_2O+CO_2+CO$$

The second reaction shows that a part of water is evolved simultaneously with degradation of oxalate ions. Sharma reported an exothermic effect in the temperature range 698–748 K. In his opinion it is related to crystallization of amorphous form of ZrO_2 directly to the monoclinic phase, in contradiction with results of Etienne *et al.* [4].

Sharin *et al.* [10] observed the formation of zirconium carbonate as an intermediate phase during decomposition of $ZrOC_2O_4$ to ZrO_2. This observation was not confirmed by other authors. The formation of $Zr(CO_3)_2$ as a transition phase is low probable, because of strong acidic properties of Zr^{4+}. More probable is, that zircon occurs in the form of basic ion ZrO^{2+}. In connection with mentioned discrepancies of opinions presented in literature we decided to re-examine this problem.

Because of practical importance of zirconia, the problem of relationships between its physical and chemical properties and conditions of preparation of $ZrOC_2O_4$ precursor seems to be particularly interesting. There are only a few communicates related to this problem. For example, in the paper of Zhang [3] the presented results show the influence of synthesis conditions on the diameter of zirconyl oxalate fine particle. In our work, apart from the ways of thermal decomposition of $ZrOC_2O_4$, we discuss correlation between the specific area of ZrO_2 (the product of decomposition) and concentration and pH of zirconyl oxychloride ($ZrOCl_2\cdot 8H_2O$) and oxalic acid solutions used in preparation of $ZrOC_2O_4$.

Experimental

Preparation

Hydrates of zirconyl oxalate $ZrOC_2O_4\cdot nH_2O$ were prepared by precipitation from water solutions of oxalic acid and zirconyl oxychloride ($ZrOCl_2\cdot 8H_2O$). The samples were obtained using solutions with three different concentrations of acid and salt: 0.5, 0.1 and 0.05 mol dm^{-3}. pH values of solutions (1, 2 and 3) for each of these concentrations were controlled by adding $NH_{3(aq)}$ or $HCl_{(aq)}$. During precipitation the solutions were stirred vigorously and pH was kept on assumed level by addition $NH_{3(aq)}$ or $HCl_{(aq)}$. The obtained white precipitates were water washed, filtered and dried at 323 K. The mass spectrometry analysis carried out during thermal decomposition of the samples showed the presence of small amount of chlorides in obtained $ZrOC_2O_4\cdot nH_2O$ (in spite of multiple washing of samples with water, what was reported also by Etienne *et al.* [4]).

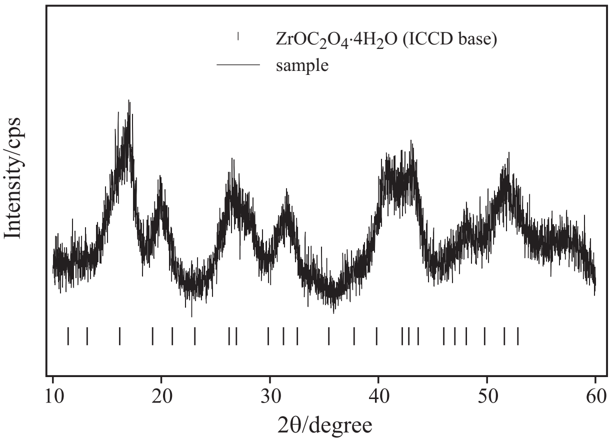

Fig. 1 X-ray diffraction pattern for initial samples

The phase composition of initial product was identified by XRD analysis. The samples of powdered zirconyl oxalate were obtained in the poorly crystalline form. XRD pattern of the dried powder (shown in the Fig. 1) is analogous to that obtained by Etienne who attributed it to a trihydrate form. However, Etienne did not describe how the water content was determined. It was probably done by taking into account the total mass loss during decomposition and assuming that molar ratio $Zr^{4+}:C_2O_4^{2-}=1$. Using the above assumption, we also obtained a mean amount mole of water per mole of $ZrOC_2O_4$, equal to three. It is necessary to emphasize that the diffraction patterns, obtained for our samples, does not correspond accurately to any diffraction pattern reported in ICCD base. It seems that the obtained results correspond better to the diffraction pattern attributed to tetrahydrate form of zirconyl oxalate. We would like to emphasise that preparation of any stable hydrate of zirconyl oxalate appeared impossible, even when the partial pressure of H_2O above the sample was controlled. Finally, we have to conclude that obtained samples are the mixture of tetrahydrate form and the other zirconyl oxalate hydrates reported in literature (1; 1.5; 3; 4; 5.5) [11–13].

A stable anhydrous zirconyl oxalate could not be obtained by drying hydrated samples at 453 K during 24 h. The mass of samples increased after taking them out of the drying chamber.

Measurements

The dehydration and decomposition of the samples were carried out in TG/DTA apparatus (SDT 2960 TA Instruments), in helium or air flow. The samples (ca. 20 mg) were heated with the rate 2, 5, 10 and 20 K min^{-1} in platinum crucible. Gaseous products of decomposition were analyzed by a mass spectrometer (Balzers, ThermoStar GSD 300 T3), connected on-line to SDT apparatus. Solid products of decomposition were analyzed by X-ray diffraction (Panalytical, serie X'Pert Pro).

The specific area of the solid products of zirconyl oxalate decomposition was determined by BET technique with N_2 (ASAP 2010 Micromeritics). The samples for BET analysis were earlier heated with the heating rate 10 K min^{-1} to 973 K.

The average diameters of crystallites of substrates and products of decomposition were determined by XRD analysis.

Results and discussion

Thermal decomposition of the gel, both in helium and in air atmosphere, proceeds in two overlapping stages (Fig. 2). The TG curves and results of analysis of gaseous products of decomposition (Fig. 3) confirmed the lack of separation between stages, which is the result of water liberation till the end of the second stage. The occluded water is probably released during the second stage of decomposition. The analogous effect was observed for the other oxalates [14–17]. It is worth to mention, that the experimental parameters can affect the decomposition process. Sometimes the changing of one parameter like heating rate or mass of sample can influence on the separating of reaction stages. We examine various conditions rate of heating (2, 5, 10 and 20 K min^{-1}) mass of sample (for example 6.5, 20, 78 mg) and carrier gas (Fig. 2). The changing of this parameters does not improve separating of stages.

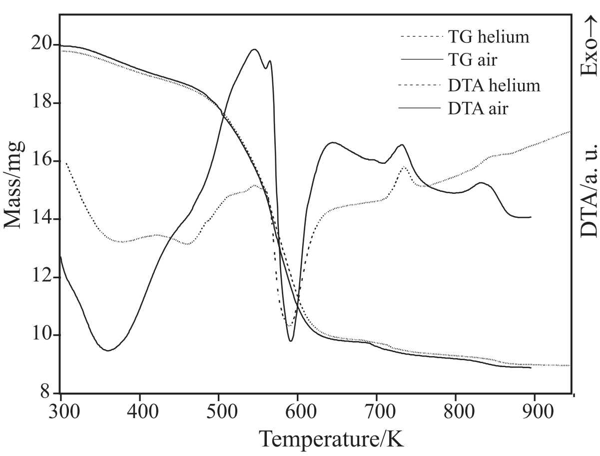

Fig. 2 Comparison TG/DTA measurements of $ZrOC_2O_4$ in air and in helium, heating rate 10 K min^{-1}

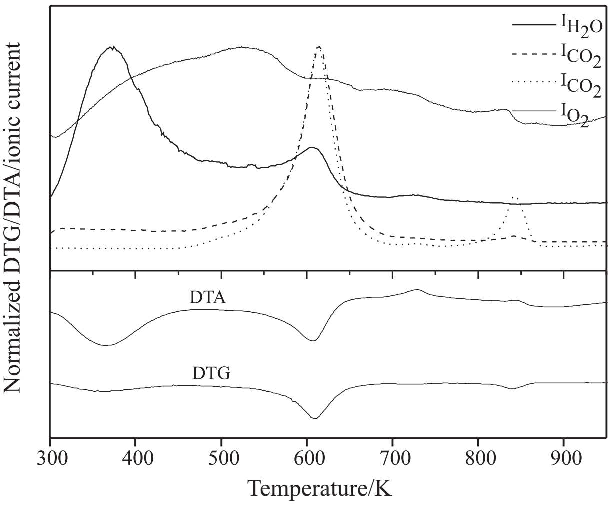

Fig. 3 Helium atmosphere, heating rate 10 K min^{-1}

Determination the amount of water evolving in the second stage using TG analysis appeared impossible. We could only estimate on the basis of EGA results, comparing surface area under ionic current issue from water (m/z=18) evolving in the first and the second step of decomposition. It was found that ratio of amount of water evolving in the first and the second step vary between 0.4 to 1.2; depending on sample. It is difficult to explain this effect. It is possible that some other factors than those which we control during synthesis are responsible for observed behaviour. Moreover, releasing of hydrogen chloride affects the mass loss.

$ZrOC_2O_4$ decomposes in the range of the temperatures 493–673 K (Fig. 2). TG curves in helium and in air are almost identical. At this stage the only gaseous product of decomposition (besides occluded water mentioned earlier) are carbon oxide and carbon dioxide. We observed ionic currents issue from m/z=44 and m/z=28, but it is necessary to emphasize that ionic current observed for m/z=28 ($I_{CO(obs)}$) is a result of CO evolution and CO_2 fragmentation during ionization in QMS ($CO_2 \rightarrow CO^+ + O^-$). The ratio of ionic current issue from CO with fragmentation of CO_2 ($I_{CO(fragm)}$) to observed ionic current issue from CO_2 ($I_{CO_2(obs)}$) is equal to 0.0658, at conditions commonly used in QMS (energy of electron ionization equal to 70 eV). So, we calculate and show ionic currents issue from gaseous product of decomposition (CO and CO_2) taking into account fragmentation, as corrected ionic currents $I_{CO(corr)}$ and $I_{CO_2(corr)}$. The comparison of corrected ionic current intensity from CO ($I_{CO(corr)}$) and CO_2 ($I_{CO_2(corr)}$) (Fig. 4) shows that the ratio of concentration of these oxides is almost equal to 1 in the mentioned above range of the temperatures. Desorption of

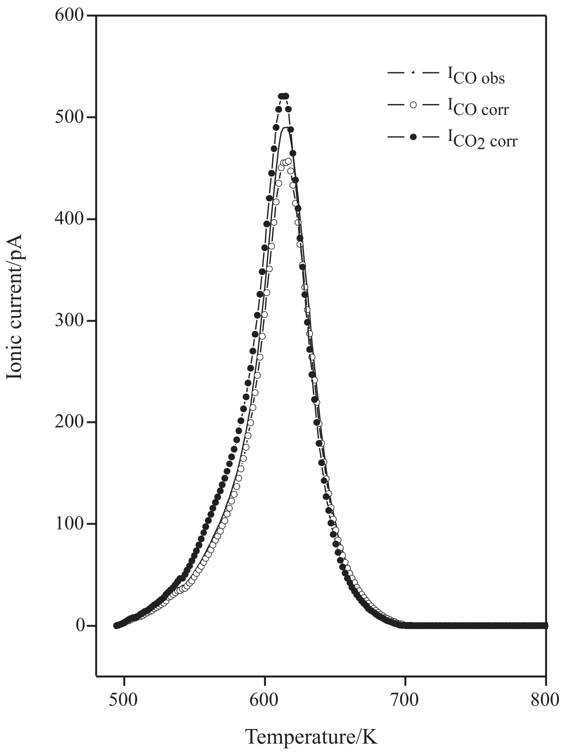

Fig. 4 Observed ionic current of CO ($I_{\mathrm{CO obs}}$), corrected ionics current of CO ($I_{\mathrm{CO(corr)}}$) and CO_2 ($I_{\mathrm{CO_2(corr)}}$) recorded during decomposition of $ZrOC_2O_4$ in helium, heating rate 10 K min^{-1}

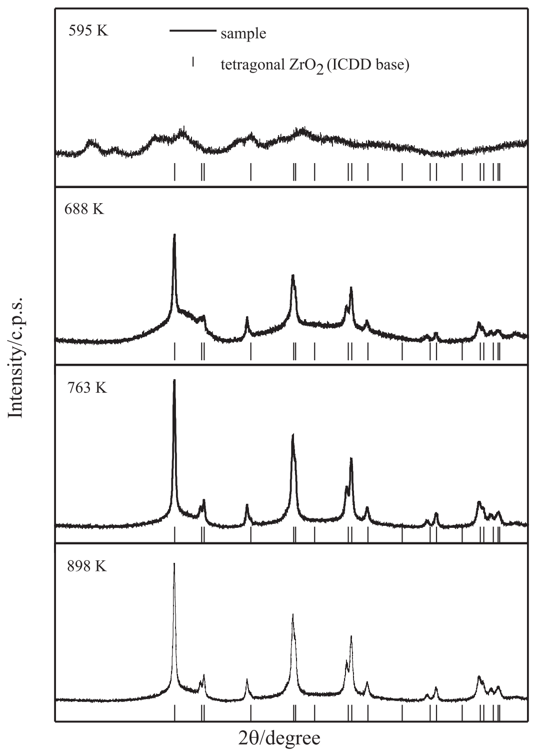

Fig. 5 XRD pattern for product of decomposition

CO_2 (which can be adsorbed on the surface of the sample during its contact with air before experiment [18]) may be responsible for releasing small amount of CO_2 earlier than CO, which appear at the beginning of decomposition.

X-ray analysis of the product of $ZrOC_2O_4$ decomposition, both in helium and in air, gives analogous results. On the Fig. 5 are shown X-ray patterns obtained for solid products of decomposition in helium. On the basis of the first pattern (obtained for sample around 595 K, when around 60 mass% of oxalate is decomposed), it can be observed, that there are not any reflexes on the diffractogram resulted from zircon oxide and X-ray pattern is rather similar to this for initial sample. It can be considered as a proof that initially ZrO_2 is created in an amorphous form. The second diffractogram (688 K) shows that tetragonal ZrO_2 appeared on amorphous background. It can correspond to formatting of zircon oxide. The next two patterns (763 and 898 K) correspond to tetragonal form of zircon oxide only. The exothermic peak on DTA curves around 723 K confirms, that crystallization takes place. EGA analysis shows that none gaseous product are evolved in this range of temperature.

Consequently, it can be concluded that decomposition of zirconyl oxalate hydrate runs in the two stages:

- decomposition of zirconyl oxalate hydrate $ZrOC_2O_4 \cdot nH_2O$ to the mixture of anhydrous $ZrOC_2O_4$ and hydrous oxalate $ZrOC_2O_4 \cdot n'H_2O$ ($n'<n$),
- decomposition of the above mixture to amorphous zircon oxide, carbon(II) and carbon(IV) oxides and water.

An exothermic peak on DTA curve (ca. 723 K) is related to crystallization of amorphous form of ZrO_2 to tetragonal form independently on atmosphere used during decomposition. The second exothermic effect can be observed around 853 K both in air and in helium atmosphere. It seems that this effect is related to oxidation of residual carbon to carbon dioxide. MS analysis shows that the ionic current corresponding to CO_2 increases in the temperature range 803–873 K, and in the same temperature region ionic current corresponding to O_2 decreases (Fig. 3). XRD analysis does not show any changes in phase composition of the sample before and after the second exothermic effect (Fig. 5). Furthermore, we can observe a small loss of mass in this range of temperature. It is also observed that the ionic current corresponding to oxygen (m/z=32) begins to decrease gradually from the temperature around 553 to the 873 K, with a significant drop around 843 K. In addition, it was observed that colour of the samples after decomposition is not clearly white, but rather grey (especially for samples decomposed in helium). It confirms that in samples heating in air, carbon is oxidized to carbon dioxide.

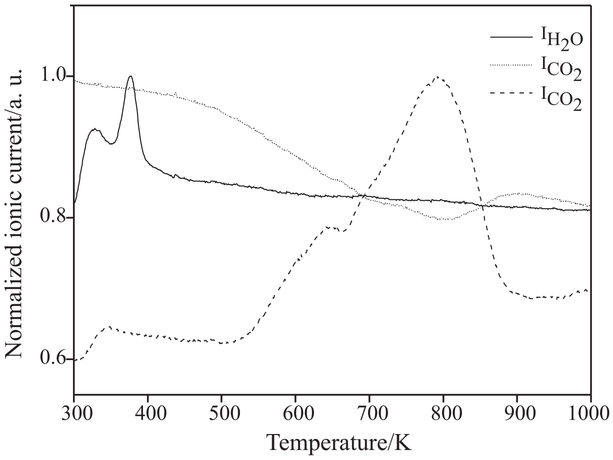

Fig. 6 Mass spectrum obtained during heating (heating rate 10 K min^{-1}) the product of the thermal decomposition of $ZrOC_2O_4$ in helium

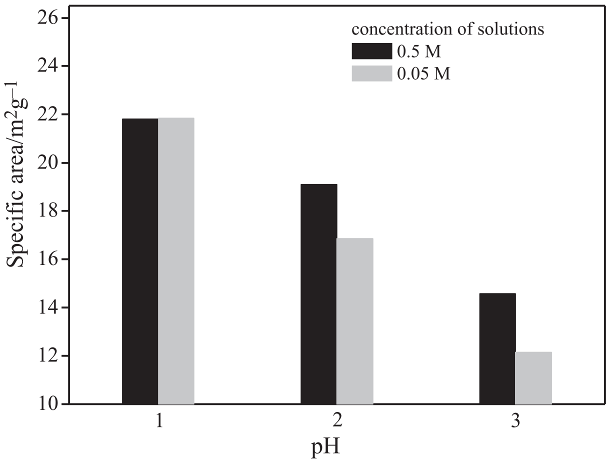

Fig. 7 Comparison of specific area for ZrO_2 obtained with different concentrations and pH of initial solutions

On the contrary, during heating in helium the amount of residual oxygen was insufficient for oxidizing carbon, which remains as a residue. In order to verify the above conclusions the heating of decomposition residue (sample was earlier heated with rate 10 K min^{-1} to 973 K in air) in helium was carried out. The EGA results are presented in the Fig. 6. The ionic currents resulting from CO_2 start to increase at the temperature 523 K, reach the maximum around 793 K and decrease to zero level around 883 K. Oxygen (the ionic current intensity corresponding to O_2 decreases) is consumed simultaneously as carbon dioxide forms. All these results confirm that small amount of carbon is formed during decomposition of zirconyl oxalate. Additionally, the compact structure of the residue and short time of the reaction with oxygen in high temperature (non-isothermal measurement with relatively high heating rate) are the reasons that a part of elementary carbon remains in the final product of decomposition after oxalate groups total degradation.

It is worth to notice, that the Boudouard's equilibrium ($2CO \leftrightarrows CO_2+C$) is thermodynamically possible in this range of temperature. Nevertheless the gaseous products of decomposition are constantly taking out by carrier gas from sample surrounding, thus the influence of this reaction on carbon contents in decomposition product seems to be negligible.

Therefore, our results seem to confirm that the favoured opinion about the second exothermic effect on DTA curves being a result of the phase transition of tetragonal ZrO_2 to monoclinic ZrO_2 is incorrect.

Microstructure observations

The relationship between specific area of ZrO_2 and the conditions of the oxalate zirconyl hydrate synthesis were found. As pH value of starting solutions increases, the specific area of the ZrO_2 powder decreases (Fig. 7). Additionally, as pH of starting solutions increases, the pore volume of the ZrO_2 powder decreases. For example, for the samples obtained from 0.05 M solutions the following values of pore volume for ZrO_2 powder were obtained (according to increasing value of pH): 10.4, 9.2 and 8.5 cm g^{-1}. This result indicates that an increase of the specific area results from an increase of powders porosity. Similar dependences of morphology and pH in synthesis of α-Al_2O_3 powders were noticed by Sharma [19]. According to this paper, pH strongly influences the structure of the initial colloid. It can be also observed, that when concentrations of starting solutions increase, the specific area of ZrO_2 also increases. This effect is not detected for ZrO_2 prepared from the starting solutions with pH equal to 1. We observed that gels prepared from the concentrated solutions precipitate immediately after stirring the solutions of precursors. The decrease of solutions concentration causes slower precipitation of gels. According to Pędzich [20] the gel derived from the diluted solution is dense as compared to that precipitated from concentrated solutions. When the process is fast (for concentrated solution as, we observed) the process results in the 'fluffy' gel microstructure. The structure of gels prepared with diluted solutions is more compact, which gives, as result of decomposition, a lower specific area than for powders precipitated from the concentrated solutions.

The crystallites size was determined on the basis of XRD-analysis. It is necessary to emphasize that monoclinic phase (baddeleit) is thermodynamically stable in the examined range of temperature to 1223 K, tetragonal phase is stable above 1423 K. Tetragonal (stable, in the room temperature) form of ZrO_2 can be also created as a result of thermal decomposition of zircon or zirconyl salts. According to Gravie [21] this effect is connected with decreasing of free surface energy of tetragonal form as compared to monoclinic.

There is a critical size of crystallites (about 10 nm), below which crystallites exist in tetragonal form.

In the case of thermal decomposition product, its crystallographic form may depend on the size of crystallites [21]. For our preparations, the size of the initial samples (colloidal particles) was around 9 nm, regardless of the conditions of synthesis applied in this work. The size of the crystallites produced at 688 K was about 12–14 nm, which is near to the critical size of crystallites proposed by Gravie.

Conclusions

Using the results based on TG, DTA, EGA, XRD, we show that thermal decomposition of zirconyl oxalate hydrate occurs in two not clearly separated stages. Initially, decomposition of $ZrOC_2O_4 \cdot nH_2O$ leads to amorphous zircon oxide with traces of carbon. Amorphous ZrO_2 transforms to tetragonal form, which is determined by the size of the crystallites. We proved that the second exothermic DTA peak is connected with oxidation of carbon to carbon dioxide, on the contrary to the literature data, where authors attributed it to transformation of tetragonal form of ZrO_2 to monoclinic. We also noticed that pH and concentrations of initial solutions (precursors) have a significant influence on specific area of obtained ZrO_2 powders. These observations can be useful in designing powders with the predicted specific area and potentially predicted sintering ability.

Acknowledgements

Authors wish to acknowledge to Polish Ministry of Science and Higher Education for financial support of this work under project No. 11.11.160.110.

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Received: November 18, 2007
Accepted: November 29, 2007

DOI: 10.1007/s10973-007-8878-x