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THERMAL DECOMPOSITION OF SEVERAL LAYERED ZIRCONIUM SALTS

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Abstract

The thermal decomposition of zirconium molybdate, tungstate and arsenate were investigated. The total mass losses of the investigated materials were 12.5, 11 and 8.5%, respectively. Despite having different crystal dimensions and structure the thermal decomposition of the samples takes place in a similar way. During heating two main endothermic processes with mass loss were observed. At the end of the thermal decomposition, oxides of the original materials were observed. The mentioned mass losses originate partly from the crystal water loss of the materials. The calculated crystal water content in the original molecule was 1.3 and 1 mole/molecule unit, respectively. Furthermore, for zirconium arsenate, a sublimation process was recorded above 960 K.

Keywords: thermal decomposition, zirconium arsenate, zirconium molybdate, zirconium tungstate

Introduction

Zirconium phosphate in various forms (amorphous and crystalline) and their derivatives or intercalates were investigated in detail [1, 2]. The thermal behaviour of this kind of materials was discussed earlier [3, 4]. Less interest has been devoted to other zirconium salts like molybdate, tungstate and arsenate. The possibility of obtaining them in well-defined crystalline form is more difficult than those of phosphates and, in addition, their ion exchange capacity is lower than that of the latter materials [5–9]. Perhaps the ‘awkward’ behaviour of these materials explains why less interest has been devoted to these zirconium salts. Bearing in mind the above mentioned factors zirconium molybdate, tungstate and arsenate in crystalline form were prepared, and subsequently identified by the XRD method with the aim of carrying out thermal analysis of the prepared materials in order to obtain more information about the thermal behaviour of these salts. Our results are presented in this paper.

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Experimental

All the chemicals used were of MERCK analytical grade production.

Preparation

Zirconium molybdate (ZrMo) was synthesized as follows: an aqueous solution of ammonium-heptamolybdate, the pH of which had previously been adjusted to 1.9 with 6 M solution of hydrochloric acid was added dropwise (at vigorous stirring) to the stoichiometric amount of zirconium oxychloride in 1 M solution of hydrochloric acid. The precipitate (amorphous gel) remained in contact with its mother liquid for 96 h at 360 K. The product was filtered, washed with redistilled water until pH=4 and it was then dried at room temperature in a vacuum dessicator over P_2O_5. The zirconium tungstate (ZrW) was prepared in the same way as described above except that ammonium-paratungstate solution was used as the starting material. Zirconium arsenate (ZrAs) was produced in the following way: 100 g of zirconium oxychloride was dissolved in 50 cm^3 1 M hydrochloric acid solution. 4 M solution of arsenic acid (120 g of As_2O_5) was added dropwise to this solution at room temperature (during continuous vigorous stirring). Furthermore, 50 cm^3 of conc. hydrochloric acid solution was slowly added. The mixture was then refluxed at 360 K for 100 h. Next, the precipitate was filtered, washed until pH=4 and dried at room temperature in a vacuum dessicator over P_2O_5.

Analytical

In the case of ZrMo, 0.2 g was dissolved in 10 cm^3 of hot conc. sulphuric acid and the solution was diluted to 200 cm^3. The molybdenum was precipitated with 5% $AgNO_3$ solution. After ignition MoO_3 was gravimetrically determined. The zirconium was also gravimetrically determined in the form of ZrO_2 from the filtrate, fuming it with conc. aqua regia and following precipitation with aqueous ammonia and ignition at 1000°C. With ZrW, 0.2 g of it was dissolved in 10 cm^3 of conc. sulphuric acid solution and then diluted to 200 cm^3. Tungsten was determined using the method described by Heyne [10], Zr as described above. In the case of ZrAs, also 0.2 g was dissolved in 10 cm^3 of 1 M solution of hydrochloric acid then the solution was diluted to 25 cm^3. As was determined iodometrically from 15 cm^3 of the previous solution; Zr was determined as described by Alberti *et al.* [11].

Identification

Sample identification was carried out by XRD method using DRON-2 type computer controlled diffractometer with CoK_α–Fe filtered radiation. The diffractograms were done in the range of $2\Theta=3–135°$ at a goniometer speed of 1° min^{-1}, then they were evaluated by a computer program [12].

Thermal analysis

A computer controlled Mettler TA-1-HT type thermobalance was used for analysis under the following conditions: temperature range 298–1023 K, heating rate= 278 K min^{-1}, gravimetric sensity=7993 units mg^{-1}, sample mass=100 mg, ambience: air (dynamic), crucible Pt, sample period 1 s.

Result and discussion

Based on the analytical data the following stoichiometric ratio was found: M/Zr=2, where *M*=Mo, W and As, respectively.

The prepared materials were identified by XRD analysis. Their possible structure and some main crystallographic data were determined and calculated, respectively based in each case on 42 peaks of the given diffractogram. The calculated data were accepted only if the results simulated with CaRine W 3.1 program were in agreement with them. The most informative fragment (in reduced form) of the given diffractograms is shown in Fig. 1.

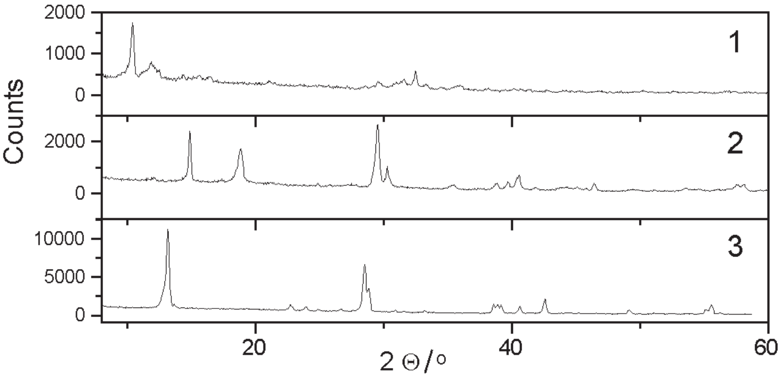

Fig. 1 A fragment of each of the X-ray diffractograms; 1 – ZrMo, 2 – ZrW, 3 – ZrAs

As a result of the evaluation, we found that all three prepared materials are crystalline. Zirconium molybdate and tungstate had a tetragonal structure (with different crystal size), and the zirconium arsenate monoclinic one. The crystal dimensions of zirconium molybdate were *a*=1.1944±0.0001 nm, and *c*=1.7870±0.0001 nm, space groups I4 c,d. For zirconium tungstate the crystal dimensions were: *a*=1.1870±0.0001 nm, *c*=1.2741±0.0001 nm, space groups I4,c,d. The dimensions of a unit cell of zirconium arsenate in space groups $P2_1/n$ are: *a*=0.5926±0.0001 nm, *b*=0.9093±0.0001 nm, *c*=1.1870±0.0001 nm, and β=101.7°. If we compare these data with that of for α-zirconium phosphate (*a*=0.9078 nm, *b*=0.5297 nm, *c*=1.5414 nm and β=101.7°, space groups $P2_1/n$ [13]), we can suppose that the zirconium arsenate also has a layered structure similarly to that of found for α-zirconium phosphate.

On evaluating the thermal analytical data we found the following:

Crystalline zirconium molybdate exhibited three endothermic processes with a mass loss of 1.1, 6.0, 3.0% and an exothermic process with a mass loss of 2.4% resulting in a total mass loss of 12.5%. The above mentioned processes take place in the temperature ranges 298–360, 470–570, 570–610 and 610–630 K, respectively (Fig. 2). As a consequence of these data, it is apparent that the first and the second endothermic processes cover parts of the crystal water loss. Based on these mass loss data one mole/molecule unit of crystal water was calculated. The third one covers the structural water loss originating from the decomposition of the molybdate part. The validity of the latter value was checked by titration of the sample with potassium ion. On the thermoanalytical curve of potassium salt for the third endothermic process a consequent lower mass loss was observed, in addition, the quantity of the exchanged potassium ion (calculated from the titration data) was found to be equal to the quantity of hydrogen ions originating from one mole of water. The exothermic process characterizes the oxygen loss taking place during the reorganization of molybdenum oxide.

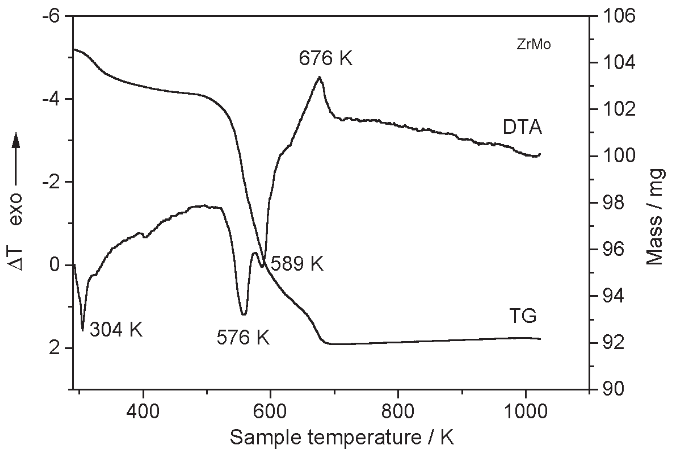

Fig. 2 TG, DTA curves of zirconium molybdate

Judging from the analytical and thermal decomposition data the initial material has the composition $ZrH_4Mo_6O_{21}\cdot H_2O$ and the final product can be characterized by the formula $ZrO_2\cdot 3Mo_2O_5$. Taking these data into consideration, the following mode of thermal decomposition can be proposed:

$$ZrH_4Mo_6O_{21}\cdot H_2O \xrightarrow[\text{up to 570 K}]{-H_2O} ZrH_4Mo_6O_{21} \xrightarrow[\text{570–610 K}]{-2H_2O} ZrMo_6O_{19} \xrightarrow[\text{up to 630 K}]{-O_2} ZrO_2\cdot 3Mo_2O_5$$

For zirconium tungstate two characteristic endothermic processes with a mass loss were observed in the temperature ranges of 370–520 and 520–690 K, respectively (Fig. 3). A total mass loss of 11% was found. Based on the analytical and thermal decomposition data the initial material can be characterized by the composition $ZrH_2W_7O_{24}\cdot 2.9\ H_2O$ and the final product identified as a mixture of oxides of

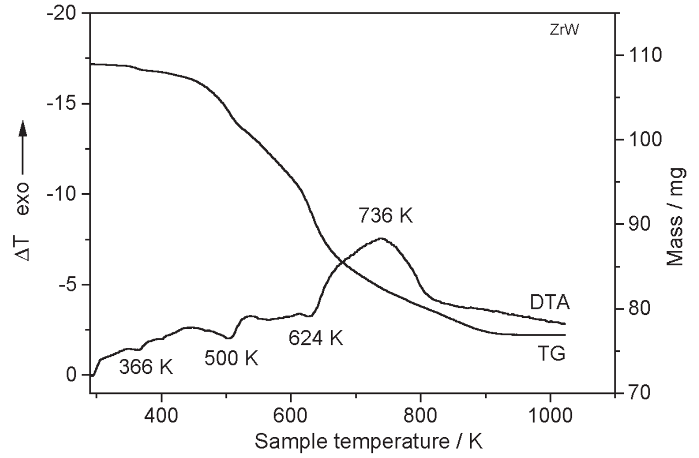

Fig. 3 TG, DTA curves of zirconium tungstate

$ZrO_2 \cdot 7WO_3$. If the sample was titrated with potassium ion the same result was found as described for zirconium molybdate.

$$ZrH_2W_7O_{24} \cdot 2.9H_2O \xrightarrow[370\text{–}520\ K]{-3H_2O} ZrH_2W_7O_{24} \xrightarrow[520\text{–}610\ K]{-H_2O} ZrO_2 \cdot 7WO_3$$

In the case of zirconium arsenate, a total mass loss of 8.5% was found, 4.0% of which belong to the first endothermic process, the second one exists in the temperature range of 450–540 K, without a mass loss, and the third one to 4.5% (Fig. 4). The analytical data of the initial product requires 31.67% of ZrO_2, 59.07% of As_2O_5 and 9.25% of H_2O. Based on these data, for the original molecule we suggest the composition $Zr(HAsO_4)_2 \cdot H_2O$, while the final product after thermal decomposition showed a mixture of $ZrO_2 \cdot As_2O_5$ (up to ~960 K), above which a sublimation process occurred. For the thermal decomposition of this material our proposition is:

$$Zr(HAsO_4)_2 \cdot H_2O \xrightarrow[\text{up to 390 K}]{-H_2O} Zr(HAsO_4)_2 \xrightarrow[450\text{–}540\ K]{\text{phase trans}} Zr(HAsO_4)_2 \xrightarrow[540\text{–}650\ K]{-H_2O} ZrO_2 \cdot As_2O_5$$

Comparison of the thermal decomposition of zirconium arsenate and α-zirconium phosphate showed considerable similarities, namely, in both cases the crystal water, one mole/molecule unit was lost (up to 420 and 430 K, respectively). This loss of crystal water is followed by a solid phase transition without a mass loss between 420–540 K and between 470–520 K, respectively. Then the materials lost their structural water in one step between 540–650 and 810–1000 K, respectively. Knowing the similarities of the crystalline structure of both materials no wonder the thermal decompositions found are almost the same for them.

Contrary to the zirconium arsenate the other two materials (molybdate and tungstate) have, as we know it from our earlier experiences, three-dimensional network structure in which the crystal water takes place likewise as it is in the layered

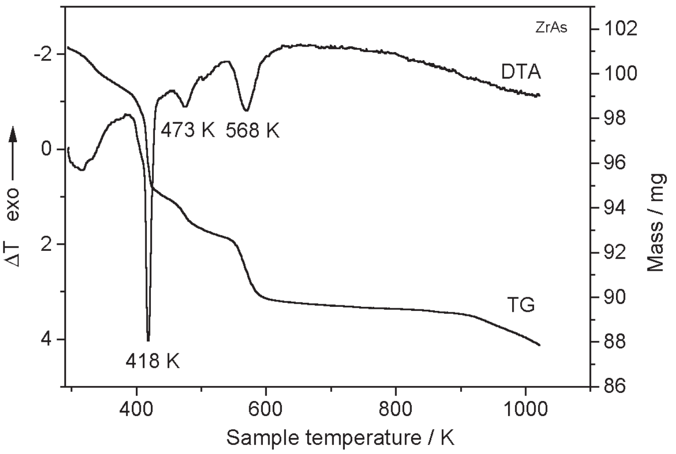

Fig. 4 TG, DTA curves of zirconium arsenate

structure. This behaviour of the crystal water can motivate the similarities found in the case of the thermal decompositions of zirconium molybdate, tungstate and arsenate regardless of the difference that exists between their crystalline structure. The similar situation of the crystal water in the structure determined in each case the first mass loss which is then followed by different decomposition, appropriate to the chemical composition of the given molecule.

Conclusions

Zirconium molybdate and tungstate have a tetragonal structure, that of zirconium arsenate is monoclinic. It means that the latter material is a crystalline monohydrogen arsenate with layered structure, similar to that of α-zirconium phosphate.

Despite having a different structure, the investigated materials showed similar thermal behaviour. They decomposed in two main steps practically within the same temperature range. During the first step they lost their crystal water without changing the crystal structure. In the second step the anionic part of the molecule is decomposed, as a result of which a water loss is observed and, finally, at the end of thermal heating a mixture of metal oxides of the original molecules remained. This phenomenon exists perhaps because of the similar position of crystal water inside the various crystalline structures. In the case of molybdate an additional oxygen loss was observed as a consequence of the reorganization of molybdenum oxide. For arsenate a sublimation process starting at about 960 K was recorded.

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