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THE THERMAL DECOMPOSITION OF ZIRCONIUM OXYHYDROXIDE

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Abstract

The thermal decomposition of zirconium oxyhydroxides prepared by the mixture of aqueous zirconium oxychloride solutions and aqueous solutions of sodium hydroxide or ammonium hydroxide under various conditions has been examined by thermogravimetry, differential thermal analysis, X-ray diffraction study and infrared spectrophotometry. As a result, it is seen that the thermal decomposition of zirconium oxyhydroxide, in which the composition is $ZrO_{2-x}(OH)_{2x}{\cdot}yH_2O$ where $x\leq2$ and $1\leq y<2$, proceeds according to the following process:

$$ZrO_{2-x}(OH)_{2x}{\cdot}yH_2O \rightarrow \text{amorphous } ZrO_2 \rightarrow$$
$$\text{metastable tetragonal } ZrO_2 \rightarrow \text{monoclinic } ZrO_2$$

Keywords: DTA, TG, thermal decomposition, zirconium oxide, zirconium oxyhydroxide

Introduction

The properties of zirconium oxide prepared by the thermal decomposition of zirconium hydroxide have been investigated by numerous researchers [1–10]. Cyprise *et al.* [1] reported a curve for the differential thermal analysis (DTA) of zirconium hydroxide exhibiting a broad endothermic reaction at 175–300°C and a sharp exothermic peak at 405°C, and interpreted the latter reaction as being due to the transformation of amorphous zirconia to the tetragonal form. Livage *et al.* [2] recognized the somewhat explosive crystallization into tetragonal zirconia at about 430°C. According to Selim and El-Akkad [3], the transformation of zirconium oxyhydroxide to amorphous oxide, viz. $ZrO(OH)_2\rightarrow ZrO_2{\cdot}H_2O$ appears as a sharp exothermic effect at 460°C, and then part of the amorphous oxide which transforms to a metastable form gives rise to the exotherm at 540°C, although the former exothermic effect is believed to be due to the crystallization of amorphous zirconia into the monoclinic form. The present author has also examined the thermal decomposition of zirconium hydroxides prepared by addition of aqueous potassium

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fluorozirconate solution to ammonium hydroxide solution. Consequently, it was found that zirconium hydroxide existing as hydrated oxyhydroxide was transformed to either the metastable tetragonal or monoclinic form via amorphous ZrO_2 [11]. However, since some discrepancies still remain in the observations of the thermal decomposition of zirconium oxyhydroxide, this paper extends the work to obtain further information about its thermal decomposition.

Experimental

A number of earlier investigators used hydrated amorphous precipitates from an aqueous zirconium oxychloride solution with ammonia. In a previous paper [11], however, zirconium oxyhydroxide was precipitated by addition of aqueous potassium fluorozirconate solution into ammonia. In the present study, zirconium oxyhydroxides were precipitated by pouring 0.2 mol dm^{-3} sodium hydroxide solution or 1.5 mol dm^{-3} ammonia at the rate of 5 mL min^{-1} up to the constant pH of 6, 7, 8, 9, 10, 11 and 12 into 20 mL of the aqueous solution containing zirconium oxychloride of 0.1 mol dm^{-1} in 0.2 mol dm^{-3} hydrochloric acid at 30, 50 and 70°C. In addition to those, zirconium oxyhydroxides were also precipitated at the same experimental conditions to the former method except for the addition of aqueous zirconium oxychloride solution to the aqueous sodium hydroxide solution. The resulting precipitates were separated by centrifugation, and washed with distilled water as free as possible from alkali metals and anions and then dried with acetone. The zirconium concentration in aqueous solution was determined by EDTA titration using xylenol orange (OX) as indicator [12].

The thermally decomposed products were prepared by heating the samples at the stated temperatures for 1 h after being heated to this temperature at a rate of 5°C min^{-1} on the basis of the results of thermal analysis.

The materials dried with acetone were examined by thermogravimetry and differential thermal analysis (TG and DTA), X-ray diffraction study and infrared (IR) spectrophotometry. TG and DTA were carried out on Shinku Riko model TGD-1500 differential thermobalance using platinum-platinum/rhodium thermocouple at a heating rate of 5°C min^{-1} in air. For the measurement of differential thermal electromotive force, α-alumina was as a reference material. X-ray powder diffractograms were obtained on Rigaku Denki diffractometer D-3F and/or using a sample heating apparatus V104627. IR spectra were determined by a Nujol or Fluorube mull method on JASCO models IR spectrometer IRA-1 and IR-F for measurements at 4000–650 and 700–200 cm^{-1} respectively, using a capillary film between thallium halide plates or polyethylene.

Results and discussion

For the precipitates from aqueous zirconium oxychloride by addition of alkaline solution, the condition of precipitation, the decomposition temperature, i.e. the peaks in the DTA curve, and the value of the molar ratio $[H_2O]/[ZrO_2]$, determined by the

Table 1 Precipitates from aqueous zirconium oxychloride solution by addition of aqueous alkaline solutions

No.	Condition of precipitation				Temp. of reaction in DTA curve/°C		Molar ratio
	[NaOH]/ mol dm^{-3}	[ZrOCl$_2$][b]/ mol dm^{-3}	pH	Temp./ °C	Endo[c]	Exo[c]	[H$_2$O]/ [ZrO$_2$]
1	0.2	0.1	6	30	80, 105	430, 432, 435	2.30
2	0.2	0.1	8	30	80, 105	422, 423, 426	2.30
3	0.2	0.1	10	30	80, 103	420, 422, 425	2.31
4	0.2	0.1	12	30	75, 103	427, 430, 435 (sh)	2.30
5	0.2	0.1	6	50	75, 110	418, 420	2.04
6	0.2	0.1	12	50	71, 106	422	2.28
7	0.2	0.1	6	70	71, 108	425, 428, 431	2.37
8	0.2	0.1	8	70	71, 103	415, 418, 420	2.27
9	0.2	0.1	10	70	71, 106	412, 415, 417	2.40
10	0.2	0.1	12	70	71, 105	430	2.41
11	(1.5)[a]	0.1	6	30	80, 106	430	2.43
12	(1.5)[a]	0.1	10	30	80, 109	416	2.11

[a] [NH$_4$OH] substituted for [NaOH].

[b] Aqueous solution containing 0.2 mol dm^{-3} HCl.

[c] Endo and exo represent the endothermic and exothermic reactions, respectively; sh denotes shoulder.

Table 2 Precipitates from aqueous alkaline solution by addition of aqueous zirconium oxychloride solution

No.	Condition of precipitation				Temp. of reaction in DTA curve/°C		Molar ratio
	[NaOH]/ mol dm^{-3}	[ZrOCl$_2$][b]/ mol dm^{-3}	pH	Temp./ °C	Endo[c]	Exo[c]	[H$_2$O]/ [ZrO$_2$]
13	0.2	0.1	6	30	85, 104	436, 438	2.75
14	0.2	0.1	8	30	80, 103	423	2.23
15	0.2	0.1	10	30	80, 104	424	2.51
16	0.2	0.1	12	30	80, 106	429	2.33
17	0.2	0.1	6	50	80, 104	425, 427	2.30
18	0.2	0.1	12	50	80, 107	426	2.18
19	0.2	0.1	6	70	85, 105	422, 424, 426	2.05
20	0.2	0.1	8	70	80, 106	424, 426	2.03
21	0.2	0.1	10	70	80, 107	424, 426	2.19
22	0.2	0.1	12	70	85, 105	428	2.12

mass loss on ignition above 100°C, are shown in Table 1. Table 2 is also indicated by the similar manner as Table 1 for the precipitates by addition of aqueous zirconium oxychloride solution to sodium hydroxide solution. TG and DTA curves for some specimens are illustrated in Figs 1–4. The phase compositions of zirconium oxyhydroxide products are deduced from the IR spectra, Figs 5–7, and X-ray diffractograms, Figs 8–9, and are presented in Table 3. Only representative IR spectra and X-ray diffractograms for the materials derived from two specimens (Nos 1 and 4) heated at various temperatures are given in these figures.

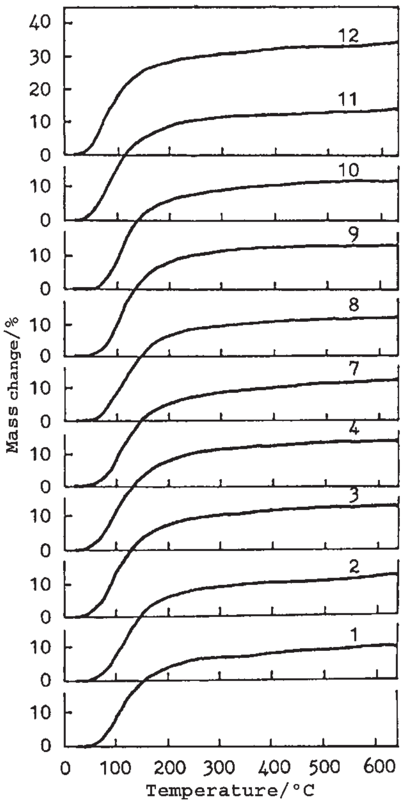

Fig. 1 TG curves for zirconium oxyhydroxides (numerals on curves represent the specimen numbers in Table 1)

From the results of the thermal analysis, it can be deduced that the thermal decomposition behaviour of zirconium oxyhydroxide precipitates occurs in two ways. The DTA curve exhibits a broad endothermic reaction centred at about 110°C, accompanied by an endothermic one which appears as a shoulder centred around 80°C, and an exothermic reaction at about 430°C. The endotherms appear at almost the same temperatures for all specimens, but the exotherms depend on the conditions of preparation of the specimens as indicated in Tables 1–2. These reactions occur at points near the change in curvature of the TG curves. In Figs 1 and 3, it is found that in the mass losses as can be observed on the TG curves of the specimens prepared by addition of sodium hydroxide solution, the loss below 100°C corresponds to nearly one molecule of water, and the loss above 100°C are less than two molecules of water. Although an additional mass loss of a few per cent is observed between 400 and 600°C, the products after dehydration reaction are supposed to exist as hydrated zirconium oxide ($ZrO_2 \cdot nH_2O$; $n<1$).

Table 3 X-ray diffraction results for the products from zirconium oxyhydroxide specimens heated at various temperatures

Temp./ °C	Specimen No.						
	1	2	3	4	7	8	9
400	*T, Am*	*Am*	*AM*	*Am*, (*T*)	*Am*	*Am*	*Am*
500	*T*, (*M*)	*T*	*T*	*T*	*T*, (*M*)	*T*	*T*
600	*T*, *M*	*T*, *M*	*T*	*T*	*M*, *T*	*T*, (*M*)	*T*, (*M*)
700	*M*	*M*, (*T*)	*M*, *T*	*M*, *T*	*M*, (*T*)	*T*, (*M*)	*T*, (*M*)

Temp./ °C	Specimen No.						
	10	11	12	13	16	19	22
400	*Am*	*Am*, (*T*)	*Am*	*Am*, (*T*)	*Am*, (*T*)	*Am*	*Am*
500	*T*	*T*	*T*	*T*, (*M*)	*T*	*T*	*T*, (*M*)
600	*T*, (*M*)	*T*, (*M*)	*T*, (*M*)	*T*, *M*	*T*	*T*, (*M*)	*T*, *M*
700	*T*, (*M*)	*M*, *T*	*M*, (*T*)	*M*, (*T*)	*T*, *M*	*T*, *M*	*T*, *M*

Am, *T* and *M* represent amorphous, tetragonal and monoclinic ZrO_2, respectively, and parenthesis denotes a small amount

On the one hand, for the specimens (Nos. 11 and 12) prepared by addition of ammonium hydroxide solution, the X-ray diffractograms reveal amorphous form; the mass losses in the TG curves correspond to the range between one and two molecules of water, and the peaks of the exothermic reactions at 430 and 416°C, respectively, in the DTA curves become smaller as well as the specimen (No. 10) prepared by addition of sodium hydroxide solution at higher pH and temperature.

As represented in Figs 8–9, the X-ray diffractograms for the precipitates of all specimens show a typical pattern of amorphous species, and at 400°C the product is crystalline. The patterns, however, are not presented, but the materials for temperatures between room temperature (air dried) and 400°C give amorphous form. In the IR spectra (Figs 5–7), the precipitates exhibit the OH stretching band (broad) with maximum at 3300 cm^{-1}, the OH bending bands at 1630, 1560 and 1340 cm^{-1} , and a broad absorption band centred around 450 cm^{-1} assigned to the Zr–O stretching frequency [10], while the heated products at 400°C show a very broad absorption band centred around 460 cm^{-1} due to the Zr–O stretching vibration of amorphous ZrO_2, although the OH absorption bands almost disappear. The Zr–O stretching band appears at 450–460 cm^{-1}, depending on the preparation conditions of the specimen. Additionally, for specimen (No. 1) prepared at low pH, the intensity of the OH absorption band at 1630 cm^{-1} is similar to that at 1560 cm^{-1}, but for specimen (No. 4) prepared at higher pH, its relative intensity at 1630 cm^{-1} is lower (Fig. 5). This tendency is also observed for other specimens. It is thus seen that the combined effect of hydrogen bonding with hydroxyl groups for the precipitate prepared at low pH is greater than that at higher pH. Accordingly, it is inferred that the composition of the precipitates is expressed as an amorphous hydrate, in which the value of $x \leq 2$ diminishes with the relation to the experimental condition to form the precipitate homogeneously from aqueous solution, and $1 \leq y < 2$ corresponding to the results of the previous paper [11]. The amorphous zirconium oxide is produced by heating the precipitates at

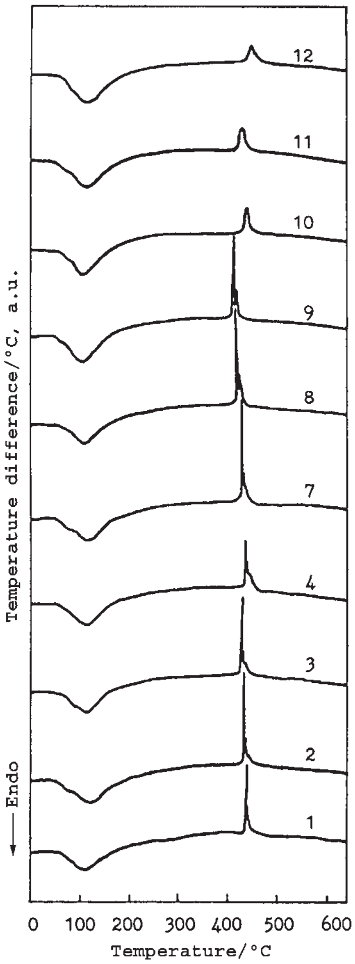

Fig. 2 DTA curves for zirconium oxyhydroxides (numerals on curves represent the specimen numbers in Table 1).

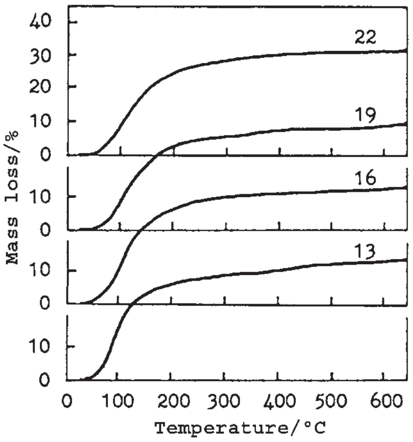

Fig. 3 TG curves for zirconium oxyhydroxides (numerals on curves represent the specimen numbers in Table 2)

200–400°C. At 500°C, the amorphous zirconium oxide crystallizes in a tetragonal phase, although some products are accompanied by a little amount of monoclinic phase (Figs 8–9 and Table 3). In any case, the major part of the products from all specimens are consisted from the tetragonal phase. A progressive increase in the intensities of the diffraction lines of tetragonal and/or monoclinic phases is observed on heating at 600°C. With further heating, the decrease in the intensity of the tetragonal diffraction lines is accompanied with increasing that of the monoclinic ones. These observations imply that the tetragonal phase formed by heating at about 500°C exists in the metastable form [8, 9] which is transformed with further heating to the stable monoclinic phase. Moreover the IR spectra for the thermally decomposed products derived from the specimens heated at various temperatures (Figs 6–7) reveal the char-

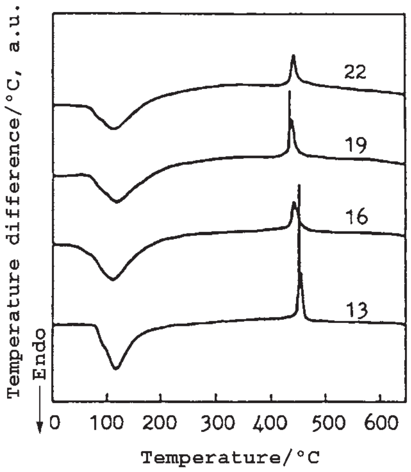

Fig. 4 DTA curves for zirconium oxyhydroxides (numerals on curves represent the specimen numbers in Table 2)

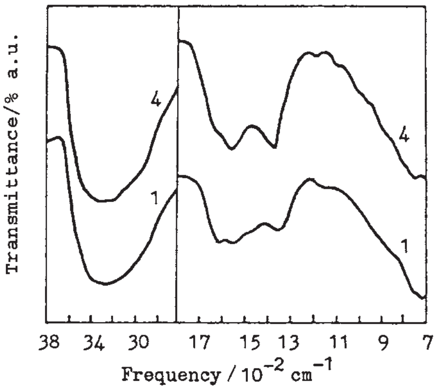

Fig. 5 IR spectra for zirconium oxyhydroxides (numerals on curves represent the specimen numbers in Table 1)

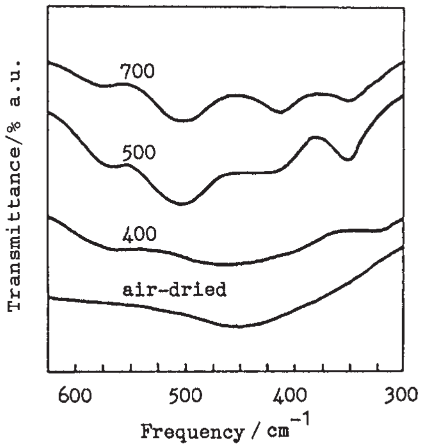

Fig. 6 IR spectra in the region of low frequency for the materials produced from zirconium oxyhydroxide heated at various temperatures (numerals on curves represent the heating temperatures, °C; for the specimen 1 in Table 1)

acteristic absorptions [6, 7, 13] corresponding to the X-ray diffraction results. On heating at 500°C, the very broad bands centred around 575, 460 and 325 cm^{-1} due to the formation of the tetragonal phase, are observed for the materials derived from specimen (No. 4) (Fig. 7), and the absorptions at 590, 510, 420 and 350 cm^{-1}, ascribed to the presence of the monoclinic phase, from that for specimen (No. 1) (Fig. 6). Therefore the following interpretation may be given for the DTA curve: the first endothermic reaction at 80°C is due to the release of adhesive water, the second endothermic reaction at about 110°C arises from the dehydroxylation during the thermal decomposition of zirconium oxyhydroxide to amorphous zirconium oxide, and the final exothermic reaction at about 430°C is attributed to the crystallization of the amorphous zirconium oxide into the tetragonal phase. This interpretation is also supported

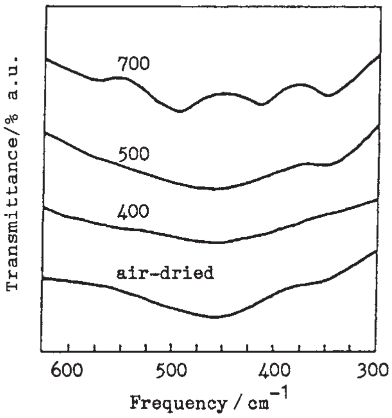

Fig. 7 IR spectra in the region of low frequency for the materials produced from zirconium oxyhydroxide heated at various temperatures (numerals on curves represent the heating temperatures, °C; for the specimen 4 in Table 1)

by the result that the molar ratio $[H_2O]/[ZrO_2]$, obtained by the mass loss deduced from the TG curve corresponds to the endothermic reaction at about 110°C in the DTA curve, is nearly two, as indicated in Tables 1–2. These observations suggest the release of about two water molecules in the thermal decomposition of zirconium oxyhydroxide.

Furthermore, X-ray diffraction study at high temperature was carried out by using sample heating apparatuses for two specimens (Nos 1 and 4). The starting materials dehydrated on heating the specimens for 1 h at 350°C were examined at different temperatures up to 800°C. In addition, when the products heated at 800°C were

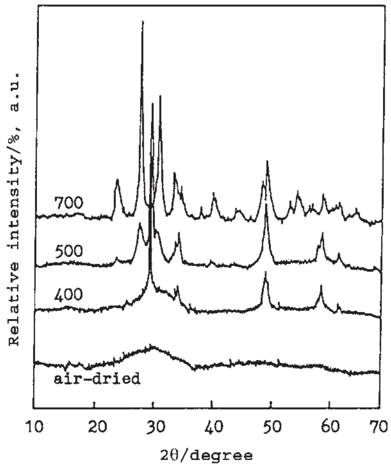

Fig. 8 X-ray diffraction diagrams for the materials produced from zirconium oxyhydroxide heated at various temperatures (numerals on curves represent the heating temperatures, °C; for the specimen 1 in Table 1)

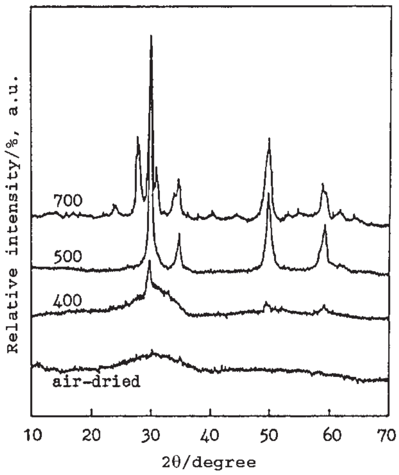

Fig. 9 X-ray diffraction diagrams for the materials produced from zirconium oxyhydroxide heated at various temperatures (numerals on curves represent the heating temperatures, °C; for the specimen 4 in Table 1)

cooled to room temperature, the materials were also examined at various temperatures. It was observed that the materials heated at 400°C reveal the pattern of a mixture of amorphous and tetragonal forms and transform to the tetragonal phase at 420°C and then the crystallization progresses with temperature. While lowering of temperature, however, the products from Nos 1 and 4 after heating at 800°C show a mixture of monoclinic and tetragonal forms at 600 and 500°C, respectively, and finally the materials transform to the monoclinic phase at 200°C and room temperature, respectively.

Hence it is concluded that the thermal decomposition of zirconium oxyhydroxide proceeds according to the scheme

$$ZrO_{2-x}(OH)_{2x}\cdot yH_2O \rightarrow \text{amorphous } ZrO_2 \rightarrow$$
$$\text{metastable tetragonal } ZrO_2 \rightarrow \text{monoclinic } ZrO_2$$

This process, depending on the composition of the original starting material, corresponds with the result for the preceding paper [11]. Similar results have also been observed for the thermal decomposition of zirconium oxyhydroxides precipitated from aqueous solution containing zirconium nitrate or sulphate by addition of sodium hydroxide solution [unpublished results].

Conclusions

It is found that the thermal decomposition of zirconium oxyhydroxides investigated by using TG, DTA, X-ray diffraction methods and IR spectrophotometry proceeds as follows:

$$ZrO_{2-x}(OH)_{2x}\cdot yH_2O \rightarrow \text{amorphous } ZrO_2 \rightarrow$$
$$\text{metastable tetragonal } ZrO_2 \rightarrow \text{monoclinic } ZrO_2$$

in which $x\leq 2$ and $1\leq y<2$, depending on the composition of the original starting material.

A similar process has also been recognized for the thermal decomposition of zirconium oxyhydroxides prepared by a mixture of aqueous zirconium nitrate or sulphate solutions and alkaline solutions.

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