LOW-TEMPERATURE PREPARATION OF TETRAGONAL ZIRCONIA ☆

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Received 25 November 1986

Tetragonal ZrO_2 has been prepared by decomposing zirconium citrate. Thermal decomposition of zirconium citrate has been studied using TG, DTA and DTG techniques. The powder X-ray diffraction studies showed that ZrO_2 prepared by this method is tetragonal up to 600°C after which it progressively transforms to the monoclinic phase. Beyond 800°C the phase is completely monoclinic. This is related to the fine particles and small crystallites obtained. The formation of metastable tetragonal ZrO_2 and its transformation to the stable monoclinic phase is studied as a function of temperature.

1. Introduction

Zirconium dioxide (ZrO_2) has three structural isomorphs. The monoclinic phase is stable below 1000°C. The intermediate tetragonal phase is stable above 1200°C and transforms to a cubic phase above 2285 ± 15°C. The transformation is reversible with a hysteresis not greater than 15°C. However, several investigators have succeeded in preparing the tetragonal form of zirconia at low temperature [1–4], which does not transform to the monoclinic phase below 600°C. Various explanations have been given for the low-temperature stabilisation of the tetragonal zirconia. Davis [3] proposed that the ZrO_2 phase depends upon the *pH* of the solutions used for the precipitation of the gels; he could obtain tetragonal zirconia from the solutions with *pH* range 3–4 or 13–14 and monoclinic in the intermediate *pH* range. Gravie [5] reported that the tetragonal form could be prepared by low-temperature decomposition of zirconium nitrate and zirconium carbonate which he explained on the basis of higher surface area. Pure and reactive ZrO_2 has also been prepared using metalorganics such as zirconium alkoxides in which metastable cubic zirconia formation has been reported [6,7]. Li et al. [8] have used zirconium citrate to prepare reactive zirconium oxide for the preparation of PLZT or $PBTiO_3$ and reported that these compounds were formed at lower temperatures as compared to the conventional techniques. The ZrO_2 obtained from zirconium citrate was found to be in the form of fine powder of high reactivity, but the details of the decomposition of the citrates and the ZrO_2 structure were not given.

In the present paper, therefore, we report the preparation of fine ZrO_2 as a result of the thermal decomposition of zirconium citrate which has been studied using the TG, DTG and DTA techniques. The structure of zirconia obtained at various temperatures has been analysed by X-ray diffraction.

2. Experimental details

Zirconium citrate was prepared using A.R. grade zirconium oxychloride and citric acid. 9.78 g of zirconium oxychloride was mixed with 7.68 g of citric acid in a beaker. While mixing, a small amount of water (≈ 5 cm^3) was added to convert the mixture to a paste-like consistency. The zirconium citrate obtained after mixing was in the form of a colourless solution. The solution was evaporated to dryness on a hot plate at a temperature of 35°C. The dried product obtained was brown in colour and glass-like in nature. This citrate product was subjected to various analytical measurements such as differential thermal analysis (DTA), infrared (IR) spectroscopy and X-ray diffraction (XRD).

The thermal decomposition study was carried out in a Netzch STA 409 differential thermal analyser

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☆ NCL Communication No. 4168.

0167-577x/87/$ 03.50

which plots simultaneously the results of differential thermal analysis (DTA), differential thermogravimetric analysis (DTG) and thermogravimetric analysis (TG) as a function of the sample temperature (T). A weighed amount of the sample to be analysed was placed in a cylindrical platinum crucible mounted on one of the 2 mm diameter alumina rods in the sample carrier covering Pt/Pt–10% Rh differential thermocouple which measured simultaneously the sample temperature. The sample was heated in a dynamic air atmosphere at a rate of 5°C/min. A chart speed of 120 mm/h was used for the thermogravimetric scan. The thermogravimetric data has been supported by infrared spectroscopy. The IR spectra of the samples were recorded on a Pye Unicam IR spectrometer (SP3-300) using Nujol as mulling agent.

For X-ray diffraction analysis, zirconium citrate was decomposed in air at different temperatures for various durations in a box-type silica furnace fitted with a chromel–alumel thermocouple for the temperature measurements. The X-ray diffraction patterns were recorded on a Philips 1730 diffractometer. Crystallite sizes were calculated from the X-ray peak width using Scherrer's equation [9]

$$D = K\lambda/\beta \cos\theta ,$$

where D is the crystallite size, K is a shape function (a value of 0.9 was used in this study), λ is the X-ray radiation wavelength (1.54 Å for Cu Kα), β is the width of the peak at half maximum (expressed in radians) and θ is the angle of incidence. β was determined from the experimental integral width by applying standard correction for the effect of Kα_1–Kα_2 separation and instrumental broadening.

Scanning electron microphotographs were recorded on a Cambridge Stereoscan-150 scanning electron microscope (SEM).

3. Results and discussion

3.1. Thermal analysis

Zirconium citrate [$Zr_3(C_6H_5O_7)_4 \cdot 4H_2O$] is found to decompose to zirconium oxide in four stages as shown in the DTA spectrum (fig. 1). The first step (step A) of the TG curve in the temperature range 25–142°C corresponds to an endothermic change leading to dehydration of the citrate molecule. The IR spectrum of the sample obtained after the first stage of decomposition is shown in fig. 2. This spectrum showed a reduction in the intensity of the broad hydroxyl band at 3400 cm^{-1} and sharpening of the bands due to citrate as compared to the starting material. The hydroxyl band at 3400 cm^{-1} at this stage is due to the –OH stretching vibration in the citrate molecule. The sharp band observed at 1580 cm^{-1} is due to the carboxylate ion in the citrate. The bands observed at 2900, 1400, 1380 and 725 cm^{-1} belong to the standard dispersing medium Nujol. The other bands observed in the spectrum are due to skeletal vibrational modes of the citrate molecule. The weight loss of 6.7% observed during this step is attributed to the removal of about 4 moles of the absorbed water.

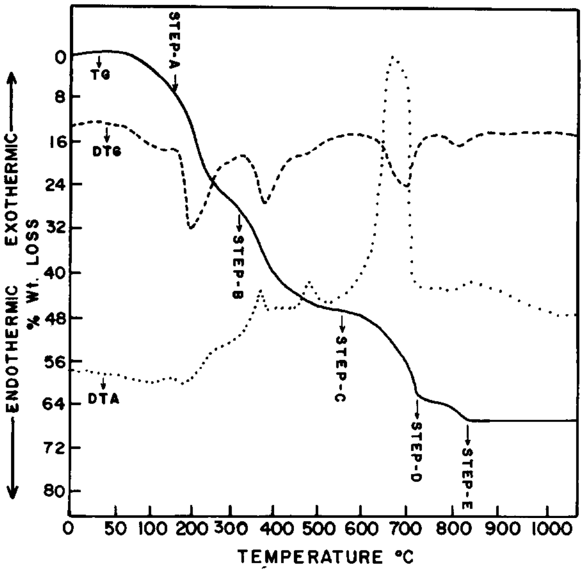

Fig. 1. TG, DTG and DTA curves of zirconium citrate in air.

The IR spectrum (fig. 2) of the sample obtained at the end of the second exothermic step (step B) in the temperature range 142–316°C showed a reduction in the intensity of the citrate bands. The intensity of the carboxylate band at 1580 cm^{-1} is reduced to 2/3 of the original value. No new bands other than the broad band at 490 cm^{-1} are observed in the spectrum. There is no indication of unsaturation, i.e. the presence of bands due to $>C{=}C<$ bonds in the IR spectrum. The band at 490 cm^{-1} corresponds to zir-

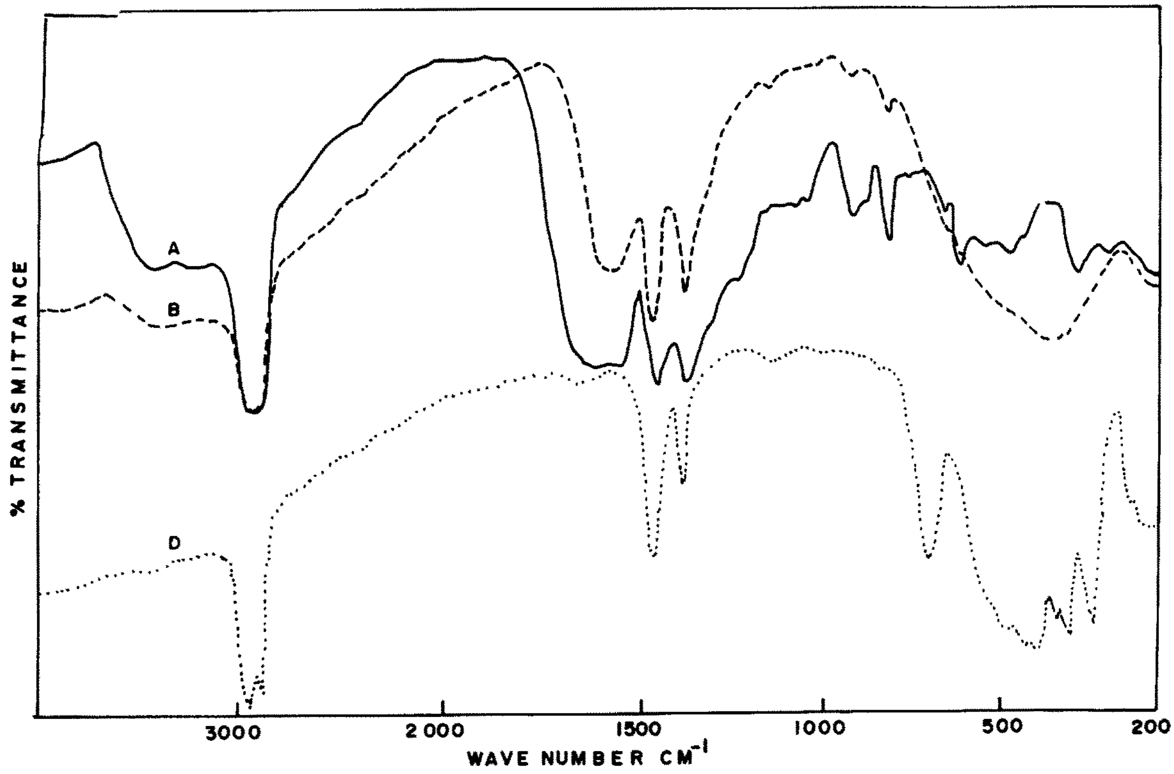

Fig. 2. IR spectra of the decomposition steps A (——), B (- - -) and D (...) of zirconium citrate.

conium oxide [10]. In this stage, therefore, partial decomposition of the citrate has taken place giving rise to the formation of tetragonal zirconia as shown in the decomposition scheme. The experimental and calculated weight loss values have been summarised in table 1.

In the third decomposition step (step C) which is exothermic in the temperature range 316–592°C further decomposition of the citrate has taken place giving rise to another molecule of zironium oxide. This was confirmed with the IR spectrum recorded for the sample obtained at the end of this stage, which showed a further reduction in the carboxylate band intensity. The IR spectrum of the sample left after the fourth decomposition step (step D) in the temperature range 592–725°C shows the complete

Table 1
Thermal analysis data for the decomposition of zirconium citrate

Decomposition step	Weight loss (%)		Temperature range (°C)	Type of reaction
	observed	calculated		
A	6.7	6.5	25–142	endothermic
B	20.8	19.96	142–316	exothermic
C	20.0	20.0	316–592	exothermic
D+E	19.1	19.95	592–840	exothermic

absence of the bands due to citrate and the presence of only the strong bands due to zirconia in the oxide region of the IR spectrum (fig. 2). Some new bands which occur at 760(m), 620(s), 535(sb) and 450(m) cm^{-1} correspond to the monoclinic form of zirconium oxide [10] instead of the tetragonal form which was present at lower temperature. The weight loss observed during this stage is, however, different from that calculated for the formation of ZrO_2. This could be attributed to the trapped CO_2 gas within the residue which escapes, later, at a higher temperature of 840°C (step E).

The above observations show that the decomposition of zirconium citrate is a gradual burning process giving the first indication of formation of tetragonal zirconia at 400°C which later transforms to the monoclinic phase at higher temperatures.

A plausible decomposition scheme of zirconium citrate may be given as follows:

$$Zr_3(C_6H_5O_7)_4\cdot 4H_2O \xrightarrow{25\text{–}142^\circ C} Zr_3(C_6H_5O_7)_4 + 4H_2O\,, \tag{1}$$

$$Zr_3(C_6H_5O_7)_4 \xrightarrow[-CO,CO_2]{142\text{–}316^\circ C} ZrO_2 + \tfrac{2}{3}[Zr_3(C_6H_5O_7)_4]\,, \tag{2}$$

$$\tfrac{2}{3}[Zr_3(C_6H_5O_7)_4] \xrightarrow[-CO,CO_2]{316\text{–}592^\circ C} ZrO_2 + \tfrac{1}{3}[Zr_3(C_6H_5O_7)_4]\,, \tag{3}$$

$$\tfrac{1}{3}[Zr_3(C_6H_5O_7)_4] \xrightarrow[-CO,CO_2]{592\text{–}725^\circ C} ZrO_2\,. \tag{4}$$

3.2. X-ray diffraction

The X-ray diffraction patterns recorded for the samples heated up to 300°C did not show any lines in the spectra. This shows that the citrate has not completely decomposed at this temperature and zirconium oxide, if formed at this temperature, is probably amorphous in nature. The XRD pattern obtained at 400°C showed the indication of the formation of crystallized zirconia in the tetragonal form [11] as shown in fig. 3A. As observed in the pattern the lines due to zirconia are not sharp thus indicating a small crystallite size for zirconia (46 Å) at this temperature. In case of the sample heated at 500°C the intensity of the X-ray peaks (fig. 3B) due to the formation of tetragonal zirconia increases with the crystallite size going up to 125 Å. This shows that by the citrate process it is possible to obtain oxides with the desired crystallite size. The XRD pattern obtained for the zirconia sample obtained at 600°C (fig. 3C) showed, in addition to the lines corresponding to the tetragonal phase, some small lines which belong to the monoclinic form of zirconium oxide [12]. The amount of the monoclinic phase increases as the temperature is increased and at 800°C (fig. 3D) the XRD pattern shows zirconia to be present entirely in the monoclinic form.

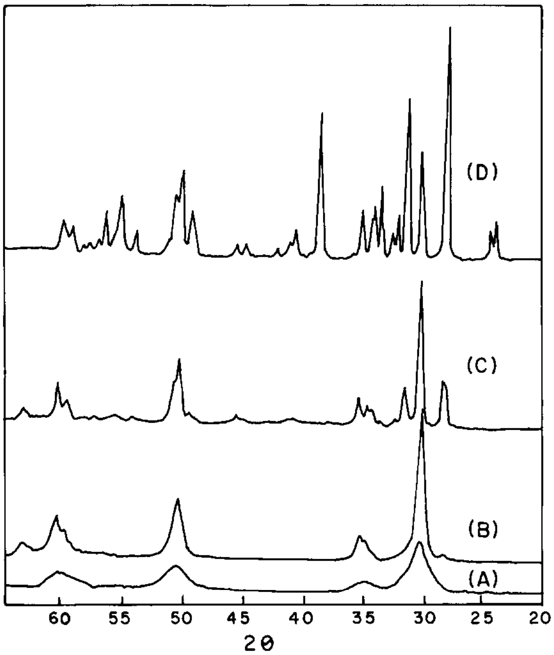

Fig. 3. X-ray diffraction pattern of zirconium dioxide obtained from zirconium citrate at various temperatures: (A) 400°C, (B) 500°C, (C) 600°C, (D) 800°C.

The above discussion shows that at lower temperature zirconia exists in the tetragonal form, the crystallinity of which increases with temperature. At higher temperature the monoclinic form is predominant.

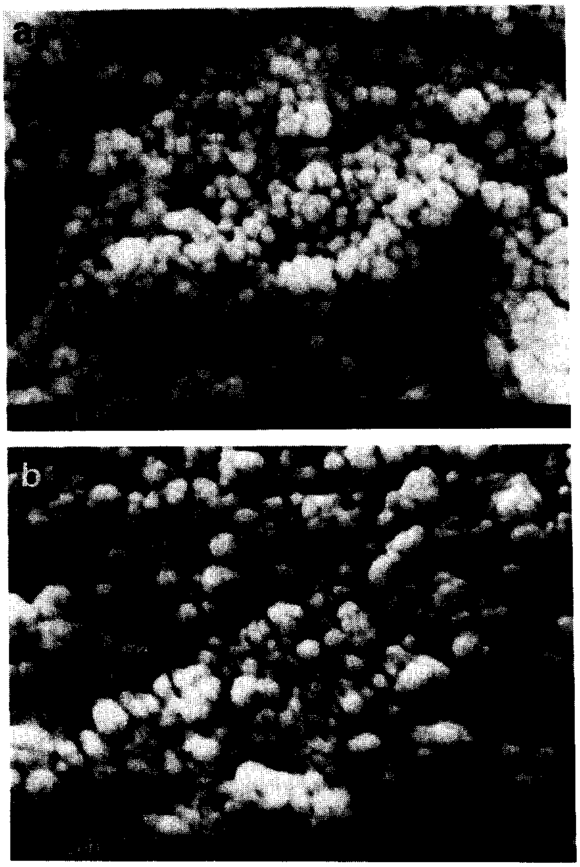

Fig. 4. Scanning electron micrographs of zirconium dioxide obtained at (a) 400°C and (b) 500°C from zirconium citrate.

3.3. Scanning electron microscopic studies

The scanning electron microphotographs were recorded for the citrate samples heated at 400 and 500°C. As can be seen in the photomicrographs (fig. 4) the particles are of submicron size, with sizes of 0.15 and 0.2 μm respectively.

The low-temperature formation of the tetragonal zirconia phase could be attributed to the fine particle size and, therefore, high surface area obtained as a result of the citrate decomposition. Thus, the small crystallite size and the *pH* of the starting material, which was found to be acidic, support the earlier reported hypothesis [3,5].

Acknowledgement

We are grateful to Dr. A.P.B. Sinha for his valuable discussions during the course of this work. We also thank Dr. V.G. Gunjikar for recording the DTA spectra and Dr. A. Mitra for recording the SEM photographs. One of the authors (AS) thanks the Council of Scientific and Industrial Research for the award of a Senior Research Fellowship.

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