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Thermochimica Acta 376 (2001) 77–82

thermochimica
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Preparation of zirconia xerogels and ceramics by sol–gel method and the analysis of their thermal behavior

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Received 11 December 2000; received in revised form 17 April 2001; accepted 19 April 2001

Abstract

Highly stable, homogeneous zirconia xerogels and ceramics were prepared from PZOs obtained by chelation of ethyl acetoacetate (Hetac) or acetylacetone (Hacac) to zirconium. The structure of PZO was analyzed by ^{1}H NMR. The thermal behavior of zirconia xerogels and ceramics were also determined by thermogravimetric/differential thermal analysis (TG/DTA), Fourier transform–infrared (FT–IR) spectroscopy and X-ray diffraction (XRD). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Xerogels; Ceramics; Sol–gel; PZO; Thermal behavior

1. Introduction

Zirconia is a multifunctional materials being widely used in optical, electronic, magnetic and thermal fields. Therefore, a lot of methods have been explored for synthesizing zirconia, including precipitation [1], sol–gel [2], thermal decomposition [3], and hydrothermal treatment [4]. Among these, sol–gel process is considered to be a promising way to produce homogeneous sols and gels with modified physico-chemical properties. The most important advantage of this method is that the synthesizing temperature is low.

In present paper, we present the using of self-produced polyzirconoxane (PZO) as the precursor to synthesize sols and gels, because it has high stability against both precipitation and hydrolysis or condensation. For these two types of PZO separately obtained from chelation of acetylacetone (Hacac) and ethyl acetoacetate (Hetac), we halve found that the latter is much easier to form gels. The explanation has obtained from the structures shown by ^{1}H nuclear magnetic resonance (NMR). The thermal decomposition was, therefore, investigated by Fourier transform–infrared spectroscopy (FT–IR), thermogravimetric/differential thermal analysis (TG/DTA) and X-ray diffraction (XRD).

2. Experimental

2.1. Preparation of PZO

Hetac or Hacac and triethylamine (0.04 mol) were added dropwise into 100 ml of methanol solution of zirconium oxychloride octahydrate ($ZrOCl_2·8H_2O$, ZOC, 0.02 mol) at 0°C with stirring. The reaction mixture was stirred at room temperature for 2 h, then concentrated. Addition of tetrahydrofuran into the residue and filtration of the resulting triethylamine

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PII: S0040-6031(01)00536-6

hydrochloride followed by concentration gave a highly viscous solution of PZO. PZO was isolated as white powders by adding the viscous solution to vigorously stirred hexane [5,6].

Thus, produced PZOs were added into distilled water to give homogeneous sols. Gels and then xerogels were obtained by evaporation of water and dried at higher temperature. And xerogels became ceramics when further calcined at 500, 900, and 1300 °C for 2 h, respectively.

2.2. ^{1}H NMR analysis

PZOs obtained separately from Hacac and Hetac were measured by using FX-90Q NMR spectrometer in chloroform-d.

2.3. Thermal analysis

Thermogravimetric (TG) analysis were performed by using American Perkin-Elmer TGS-2 in air dynamic atmosphere with a flow rate of 50 ml min^{-1} at a heating rate of 20°C min^{-1} over the range 50–760°C and using 8.2 mg of sample in an aluminum cell. The differential thermal analysis (DTA) was performed on American Perkin-Elmer DTA1200. DTA curve was obtained in air dynamic atmosphere with flow rate of 50 ml min^{-1}, with masses of 15 mg at a heating rate of 20°C min^{-1} from 50 to 1000°C. The reference was a pure aluminum cell.

2.4. Infrared transmittance spectrum

Infrared spectrum was recorded by an FT–IR spectrometer (American Ncolet FT–IR 20SX).

2.5. X-ray diffraction

X-ray powder diffraction patterns were obtained by using a Japan/D model Max-•=A6=C3AA.

3. Results and discussion

3.1. Gels formation from two different types of PZOs

Both Hacac and Hetac are effective ligands chelated to zirconium to get stable sols and gels against precipitation, and they strongly restrain both hydrolysis and condensation. For these two ligands, the latter is much easier to form gels. Table 1 shows that the formation time of gels from PZOs is depending on chelating ligands.

Table 1
Time of the formation of gels at 60°C

Sample number	Chelating ligand	Chelating ligand/Zr (molar ratio)	Gels formation time
1	Hetac	1:1	Several minutes
2	Hetac	1:1.5	2 days
3	Hacac	1:1	14 days
4	Hacac	1:1.5	4 months

From the above table, we can see that Hacac is obviously a much stronger chelating ligand than Hetac.

The ^{1}H NMR spectrum of PZO derived from Hetac (Fig. 1) indicates that the signals shown by the ethyl acetoacetato group are at 1.2 (CH_3CH_2O–), 1.8 (CH_3CO–, enol form), 2.2 (CH_3CO–, keto form), 3.3 (–CH_2–, keto form), 3.8 (=CH–, enol form) and 4.8 ppm (–OH), respectively, whereas in the ^{1}H NMR spectrum of PZO derived from Hacac (Fig. 2), there are signals shown by the acetylacetonato group at 1.5 (CH_3CO–, enol form), 2.1 (CH_3CO–, keto form), 3.3 (–CH_2–, keto form), 3.6 (=CH–, enol form) and 5.5 ppm (–OH), respectively.

The enol form of Hetac or Hacac is easily to chelate to zirconium, thus largely reduces the tendency of zirconium to form bulk gels and enhances the stability of sols. The reason why PZO sols derived from Hacac is more stable lies in the fact that at room temperature, Hacac consists of 15% keto form, and 85% enol form easy to chelate, whereas in Hetac, it consists of 92.5% keto form, and only 7.5% enol form [7,8].

The structure derived from ^{1}H NMR spectrum of PZO (taking Hetac chelated as an example) is shown in Fig. 3 [9].

3.2. Thermal behavior and characterization

3.2.1. Thermal behavior

From the TG/DTA curves (Fig. 4), the sample resulted from gelation of acetylacetone chelated

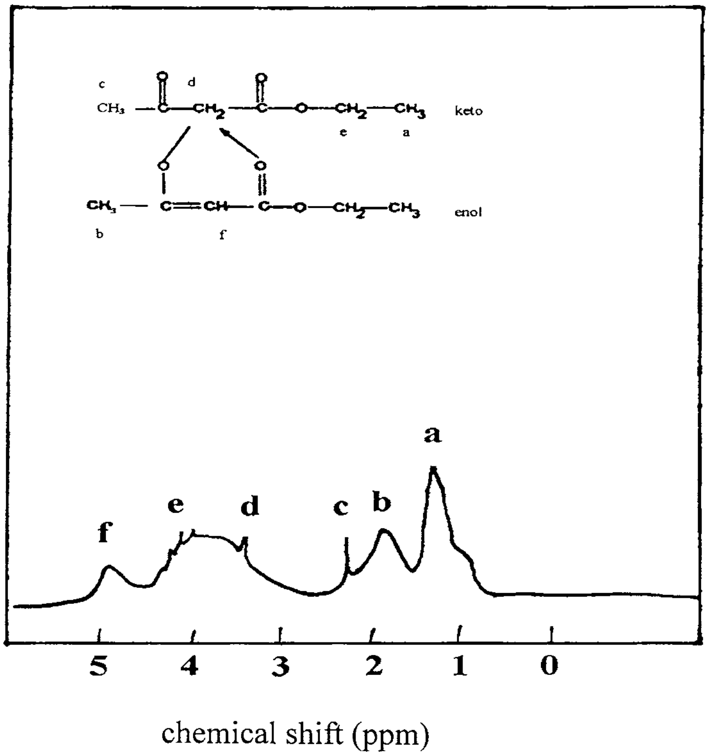

Fig. 1. ^{1}H NMR spectrum of PZO derived from Hetac.

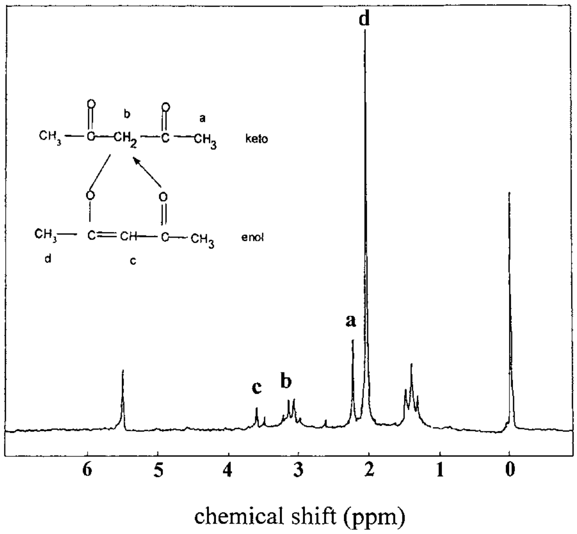

Fig. 2. ^{1}H NMR spectrum of PZO derived from Hacac chemical.

PZO shows a weight loss at 50–250, 250–400 and 400–600°C, corresponding to one endothermic and two exothermic peaks, respectively. The peak at 50–250°C should correspond to the desorptions of both physically-absorbed water and solvent, the exothermic peak at 250–400°C could be caused by the oxidative

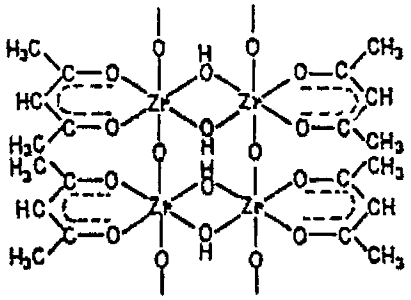

Fig. 3. Structure of PZO chelated by Hetac.

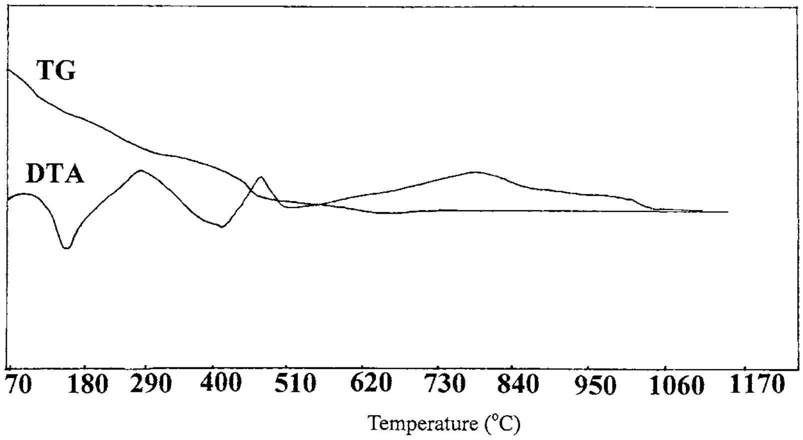

Fig. 4. TG/DTA curves of PZO xerogels.

decomposition of organic residues, and the peak at 400–600°C might correspond to the dehydroxylatin of Zr–OH into ZrO_2 [10].

In the DTA curve, there is also a wide weak exothermic peak from 700 to 1000°C, which could be caused by the growth of zirconia crystal size. This could be tested by the XRD pattern in Section 3.2.3.

3.2.2. *Characterization of IR*

The IR spectrum of PZO xerogels at 100°C (Fig. 5) exhibits transmittance peaks at 3400 (•OH), 3000 (•CH), 1580 (•C=O), 1530 (•C=C), 1280 (•CCH_3) and 460 cm^{-1} (•Zr–O), respectively [6]. While the IR spectrum of xerogels or ceramics dried at 180, 300, 500, 900, 1300°C shows successively decrease in the

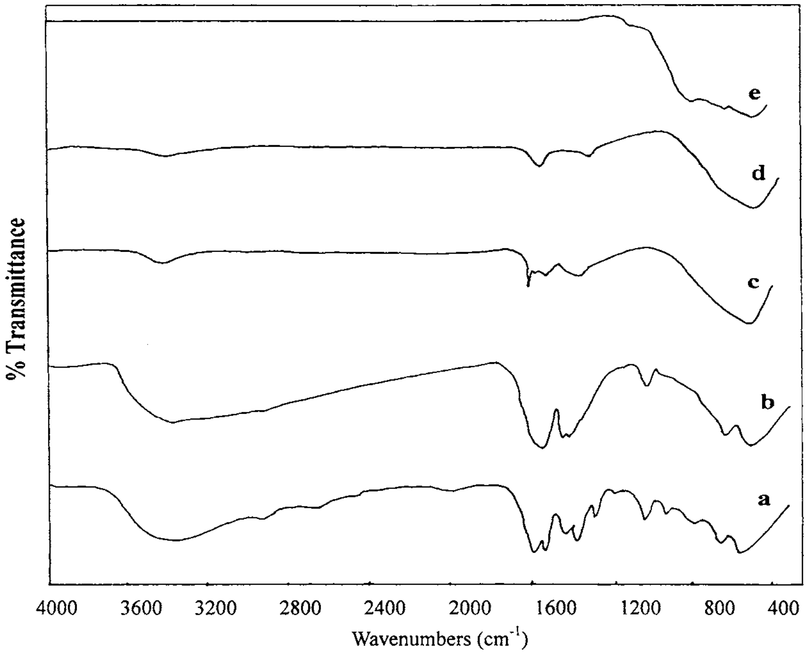

Fig. 5. IR spectrum of PZO xerogels or ceramics xerogels or ceramics dried at: (a) 60; (b) 180; (c) 300; (d) 500; and (e) 900°C for 2 h.

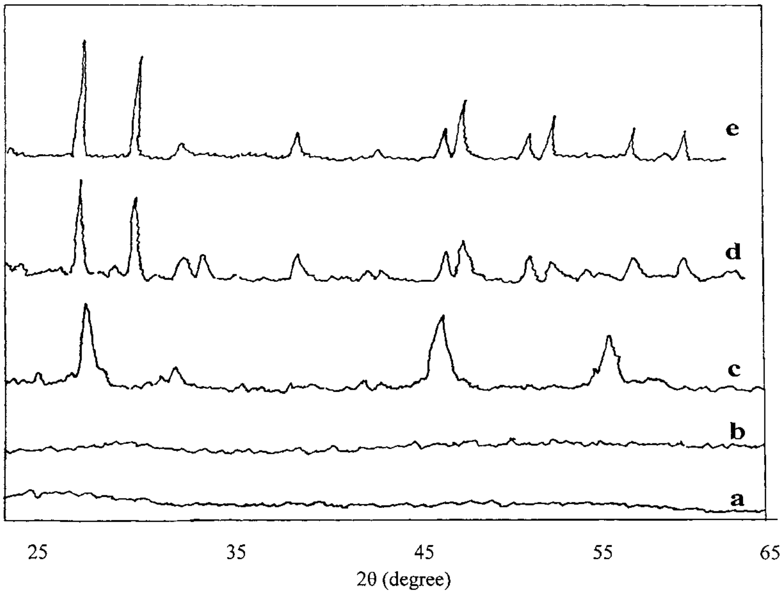

Fig. 6. XRD pattern of PZO xerogels or ceramics xerogels or ceramics dried at: (a) 100; (b) 300; (c) 500; (d) 900; and (e)1300°C.

number of peaks, which is in good agreement with the desorption, decomposition and dehydroxylation mentioned in Section 3.2.1.

3.2.3. XRD pattern of the xerogels or ceramics

The XRD patterns of the xerogels or ceramics at different temperatures are shown in Fig. 6. The products at 100 and 300°C are amorphous to X-rays, and are crystallized in tetragonal or monoclinic zirconia after heat treatment at 500°C for 2 h. The crystallinity of zirconia increased with the increasing of heat-treatment temperature from 500 to 1300°C, also shown in Fig. 6. From the XRD pattern, zirconia particles are believed to be of sub-micrometer size [11].

4. Conclusions

Highly stable, homogeneous zirconia xerogels and ceramics can be prepared from PZO. The formation and thermal behavior are summarized as follows:

1. The chelation of enol form of Hetac or Hacac with zirconium strongly restrains both hydrolysis and condensation and then the stability is highly improved.
2. The thermal behavior of PZO xerogels consists of three stages, such as loss of water and solvent, decomposition of organic residues and dehydroxylation of Zr–OH into ZrO_2.
3. The ceramics obtained above 500°C consist of sub-micrometer sized zirconia particles.

Acknowledgements

This paper is sponsored by natural science foundation of China. The number is 50072012.

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