Thermochimica Acta 473 (2008) 81–85

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal behavior of polyacetylacetonatozirconium (PAZ)

L.Y. Zhu*, G. Yu, X.Q. Wang, X.Q. Hou, X.J. Liu, J. Sun, Z.H. Sun, H.L. Fan, D. Xu*

State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 7 March 2008
Received in revised form 17 April 2008
Accepted 19 April 2008
Available online 2 May 2008

Keywords:
Polyacetylacetonatozirconium (PAZ)
Thermal behavior
Thermogravimetry/differential thermal analysis (TG/DTA)
Fourier transform infrared spectroscopy (FT-IR)

ABSTRACT

The thermal behavior of polyacetylacetonatozirconium (PAZ) was characterized by thermogravimetry–differential thermal analysis–derivative thermalgravimetric (TG–DTA–DTG) techniques. The thermal decomposition studies under air, N_2 flux and N_2 flux after pretreated by steam showed different thermal behavior modes. Further investigation revealed that the steam pretreatment had extraordinarily significant effects on the thermal behaviors of PAZ. X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FT-IR) were used to indicate the morphology form and confirm the composition of PAZ during the heat-treatment.

1. Introduction

In our group earlier studies relating to the preparation and characterizations of polyacetylacetonatozirconium (PAZ) were reported [1] and the preparation of zirconia xerogel and ceramics and their thermal behaviors were studied [2]. Because of the high melting temperature of zirconia, the zirconia fiber was fabricated mainly by sol–gel and polymer-derived routes [1,3–7]. The thermal decomposition of the precursors is an important stage of all "wet" synthesis techniques, because it determines a number of properties of the final product, including the stoichiometry, porosity, size of the pores, mechanical properties and specific surface area. The transformation of the precursor to the polycrystalline zirconia fibers is complicated and the mode of the thermal decomposition of the polymer plays an important role in the physicochemical properties of the zirconia fibers. To our best knowledge, the thermal decomposition processes are affected by the ambience and heat-treatment system obviously. Our group has studied the formation pathway and the effects of the heating condition on the preparation of zirconia fibers from a spinning solution and their physical properties and micro- and macrostructures were affected severely [1]. Therefore, the thermal behavior and heat-treatment conditions are very important for the high quality zirconia fibers.

Methods of thermal analysis have made great progress during the last decades and have found wide spread practical applications. Nowadays, these techniques are important tools in research and routine analysis. Thermogravimetry/differential thermal analysis (TG/DTA) is valuable technique for the study of the thermal properties of various compounds [8–11]. In this paper, the thermal behavior of PAZ was analyzed. The significant effects of steam pretreatment on the decomposition process of PAZ were discussed based on the experimental results. In this study, TG, DTA, X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FT-IR) were utilized to accomplish our aim.

2. Experimental

2.1. Preparation and the molecular structure of PAZ

The preparation and structural characterization of PAZ have been reported in the early report [1]. The precursors were pretreated under normal pressure steam by electric saucepan with 1 h, 3 h, 4.5 h, 6 h and 7.5 h, respectively, and then rubbed into powders for the measurements. The molecular structure of PAZ was determined by FT-IR, ^{1}H NMR, and EA (element analysis) and presumed as a linear –Zr–O–Zr– double-chain polymer structure, each Zr connected to three –OH groups and one acetylacetone, Zr and Zr were connected with each other by means of the bridging function of –OH group to form a double-chain polymer, acetylacetone was served as pendant group and formed a six-member ring with Zr.

---

* Corresponding authors.
E-mail addresses: zhuly@icm.sdu.edu.cn (L.Y. Zhu), xdoffice@sdu.edu.cn (D. Xu).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.04.016

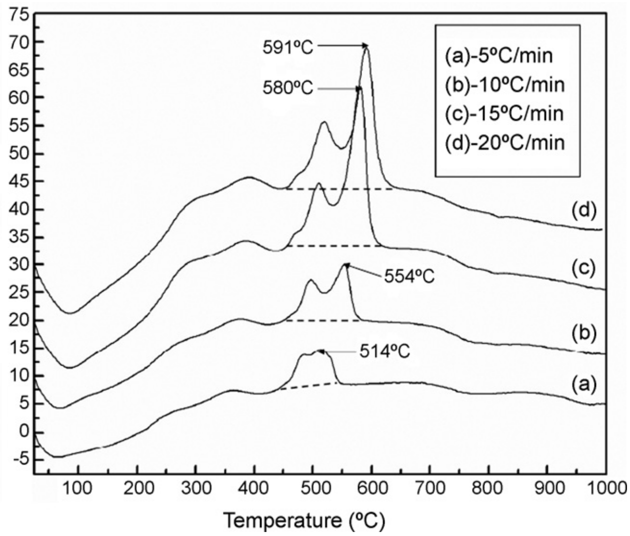

Fig. 1. DTA curves of PAZ at different heating rates under air flux.

2.2. *Measurements and characterizations*

The raw and pretreated precursors and the samples sintered at different temperatures were rubbed into powders for TG/DTA, XRPD and FT-IR measurements.

The TG/DTA measurements were carried out from 25 °C to 1000 °C by using a Diamond TG/DTA PerkinElmer instrument under air flux at different heating rates, 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively. The TG–DTA–DTG measurements were carried out in the temperature range of 25–600 °C at the heating rate of 10 °C/min under N_2 flux. The TG/DTA measurements for the pretreated precursors at different time were implemented by the above thermal analysis instrument ranging from 25 °C to 1000 °C at the heating rate of 10 °C/min under N_2 flux. The samples were weighed on a platinum crucible with a microprocessor-driven temperature-control unit and a data station.

The crystallite structure of the sample was analyzed by XRPD with a Bruker AXSD8 Advance X-ray diffractometer, operated at 40 kV and 40 mA, using Cu Kα radiation ($\lambda = 0.154178$ nm) and a graphite monochromator. Intensity for the diffraction peaks were recorded in the 15–60° (2θ) range with a step size of 0.02°.

The measurements of the FT-IR spectra were done using KBr pellets on a Nicolet 170sx FT-IR spectrometer ranging from 400 cm^{-1} to 4000 cm^{-1}.

3. Results and discussion

3.1. *Thermal decomposition of PAZ under air flux*

The general DTA curves at different heating rates of PAZ under air flux were shown as Fig. 1. Below 470 °C, including the decomposition of the chelate acetylacetone and the reaction can be written in the present case as

$$\mathrm{PAZ(Zr(OH)_3(acac))} + \mathrm{O_2} \rightarrow \mathrm{ZrO_2} + \mathrm{CO_2} + \mathrm{H_2O}$$

Because the isolation of PAZ and triethylamine hydrochloride were used tetrahydrofuran, very little triethylamine hydrochloride was inevitably residued in the PAZ/tetrahydrofuran solution. Below 100 °C, there was a small endothermal peak according to the removal of the triethylamine hydrochloride and tetrahydrofuran. During the combustion, may be acetylacetone ligand was burned out firstly, and the hydroxyl groups still existed from the FT-IR spectra (Fig. 2) of PAZ heat-treated at 450 °C. Besides hydroxyl groups, the vibration of C=C, C=O and deformation mode of the acetate groups at 1535 cm^{-1}, 1450 cm^{-1} and 644 cm^{-1}, respectively, were also observed in Fig. 2 (450 °C). The maximum exothermal peak at 470–600 °C might mainly correspond to combustion of the residual ligands and accompanied by the dehydroxylation of Zr-OH into ZrO_2 [12–14]. The peaks shifted to high values from 514 °C to 591 °C and the completely decomposition temperature was shifted to higher values with the heating rate increasing. Therefore, slow heating rate was necessary for obtaining high quality zirconia fibers. Fig. 3 shows the TG/DTA curves of PAZ at the heating rate of 10 °C/min under air flux. As may clearly be seen from Fig. 3, the mass of the measurement sample was decreasing homogeneously before 600 °C. Below 470 °C, the mass loss was about 40% including removal of the triethylamine hydrochloride and tetrahydrofuran and the combustion acac group. In the temperature range 470–600 °C, about 10% mass loss was observed mainly corresponding to combustion of the residual ligands. In the temperature extent, the decomposition of organic group and the nucleation of zirconia and grain growth were included. Fig. 4 displays XRPD patterns of PAZ heat-treated at different temperatures under air flux. The unpretreated precursor and the product at 200 °C were amorphous, and were crystallized in tetragonal zirconia phase after heat-treated at 400 °C. It means that some zirconia nucleus have been formed at 400 °C and grown with the increasing of the temperature.

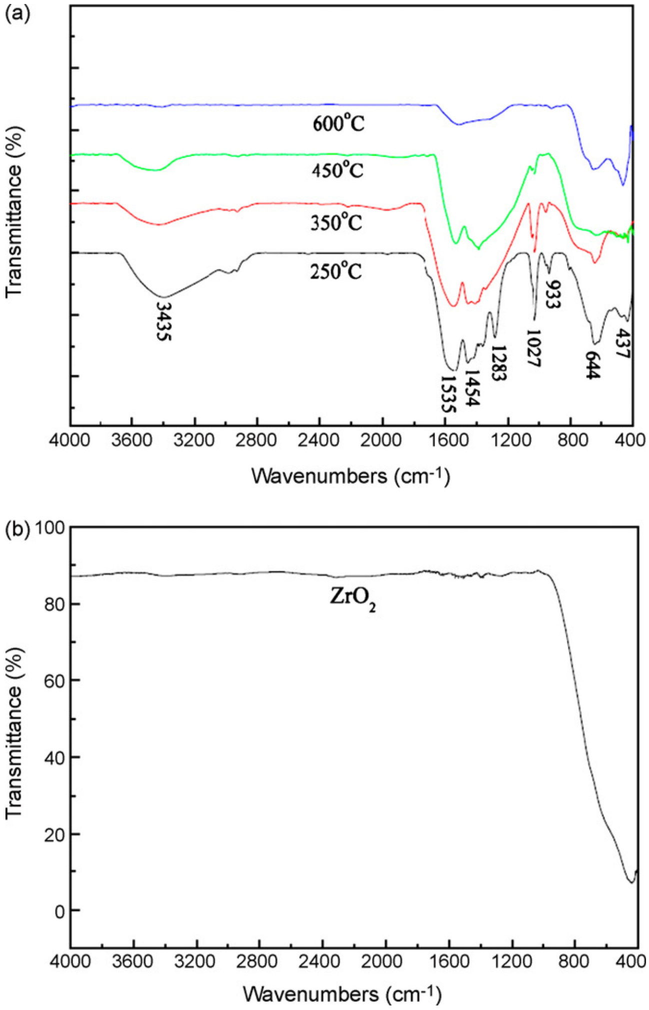

Fig. 2. (a) FT-IR spectra of PAZ heat-treated at different temperatures in air; (b) FT-IR spectrum of pure ZrO_2.

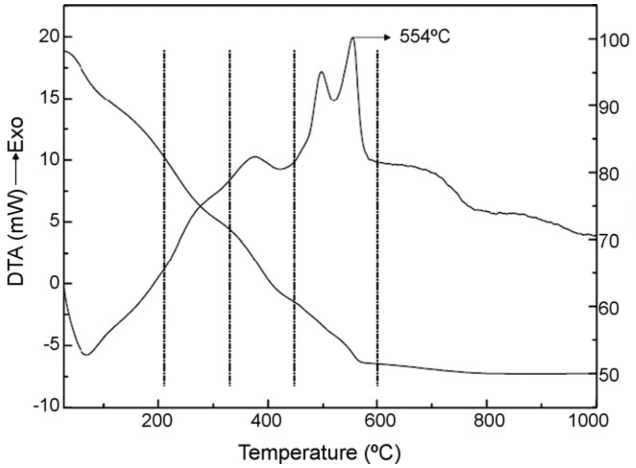

Fig. 3. TG/DTA curves of PAZ at the heating rate of 10 °C/min under air flux.

FT-IR spectra of PAZ heat-treated at different temperatures were shown in Fig. 2(a). The FT-IR spectrum of PAZ precursor exhibits transmittance peaks at 3400(υ_{O-H}), 3000(υ_{C-H}), 1568($\upsilon_{C=O}$), 1535($\upsilon_{C=C}$), 1450 ($\upsilon_{C=O}+\delta_{C-H}$), 1228$_{(\upsilon(C-CH_3))}$, 1032$_{(\pi(CH_3))}$ and 400–500 cm^{-1} (υ_{Zr-O}), respectively [15]. The intensity and number of the peaks were decreasing with the temperature increasing. The band associated with the vibrational mode of the skeletal O—Zr—O bonds of ZrO_2 appeared ranging from 400 cm^{-1} to 500 cm^{-1} as shown in Fig. 2(b). After heat-treated at 600 °C, all strong organic parts are removed. No signs of adsorbed water or hydroxy, carbonate or hydrocarbon impurity can be observed. This is due to the formation of zirconia, which is good agreement with the results of XRPD and TG/DTA.

3.2. *TG–DTA–DTG analysis under N_2 atmosphere*

The TG–DTA–DTG curves of PAZ heat-treated at heating rate of 10 °C/min under N_2 flux were exhibited in Fig. 5. The TG and DTA curves revealed that the ligands acetylacetone decompounded in three stages in the temperature range 100–600 °C. Below 100 °C, there is a mass loss about 5% in TG curve, corresponding to an endothermal peak in the DTA curve, due to the removal of the triethylamine hydrochloride, tetrahydrofuran and the adsorbed volatile matters. The first step in the decomposition of PAZ (100–300 °C) is accompanied by exothermic effects in the DTA curve with the evolution of little half of the acetylacetone ligands from the complex and the mass loss was about 15%. The second step of the mass loss is about 23% in the TG curve, in the temperature range of 300–450 °C, without apparent endothermal or exothermal peaks in the DTA curve. The loss is very apparent during 350–450 °C, corresponding to the removal of the some organic ligands. Synchronously, the crystal nucleus of zirconia is formed. There is about 5% loss in the last step (450–550 °C) in the TG curve accompanied by an exothermal peak in the DTA curve, due to the formation of the polycrystalline zirconia. The position of the exothermal peak shifted to lower temperatures compared with that of Fig. 3. This means that the inert (N_2) atmosphere is in favor of the decomposition of PAZ and the transformation from PAZ to ZrO_2 at lower temperature.

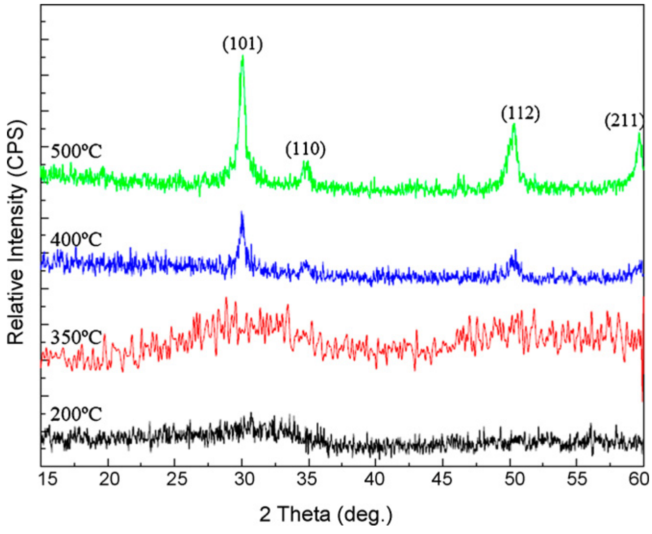

Fig. 4. XRPD patterns of PAZ heat-treated at different temperatures under air flux.

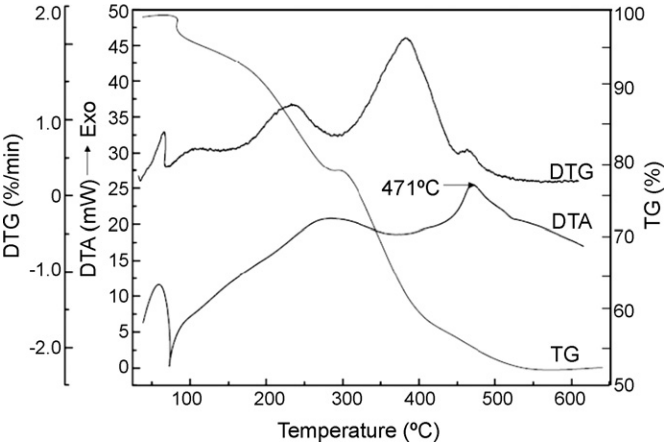

Fig. 5. TG–DTA–DTG curves of PAZ heat-treated under N_2 flux.

3.3. *Influence of steam pretreatment on the PAZ decomposition under N_2 atmosphere*

Fig. 6(a–e) displays the TG/DTA curves of PAZ pretreated under normal pressure steam at 1 h, 3 h, 4.5 h, 6 h and 7.5 h, respectively. Seen from Fig. 6, there are about two apparent steps in TG curves after steam pretreatment, which is different from Fig. 3. The first step is about the vapor volatilization at 100–200 °C, corresponding to the endothermic peak in DTA curves. The second one is at about 450–500 °C, but apparent endothermic or exothermic peaks were not observed in the DTA curves around the temperature extent. There is an apparent exothermal peak at around 220 °C (See Fig. 6(a) and (b)), probably due to the removal of the acac groups. This clear exothermal effect disappears when the pretreatment time increases. For zirconia fibers, Abe and coworkers [16] have described that the steam treatment of the green fibers was very effective in obtaining oxide fibers with an appreciable tensile strength because hydrolysis of the ligand group leaded to a reduction of the stress evolved on combustion of the organics. Due to the pretreatment, the mass loss is vicissitudinous and the mass of the final residue is between 35 and 60% of the mass of the origin compound. And the TG curves cannot be used to explain the mass loss of the origin compound. Comparing to Figs. 3 and 6, the shapes and the peak positions of the DTA curves were changed apparently. Exothermic peak at 450–500 °C becomes weak even disappeared after pretreated under steam pretreatment. This founding makes the assumption that the organic parts were combusted in air flow and changed into H_2O and CO_2; differently, displacement reactions were occurred between steam and the organic ligands. The sup-

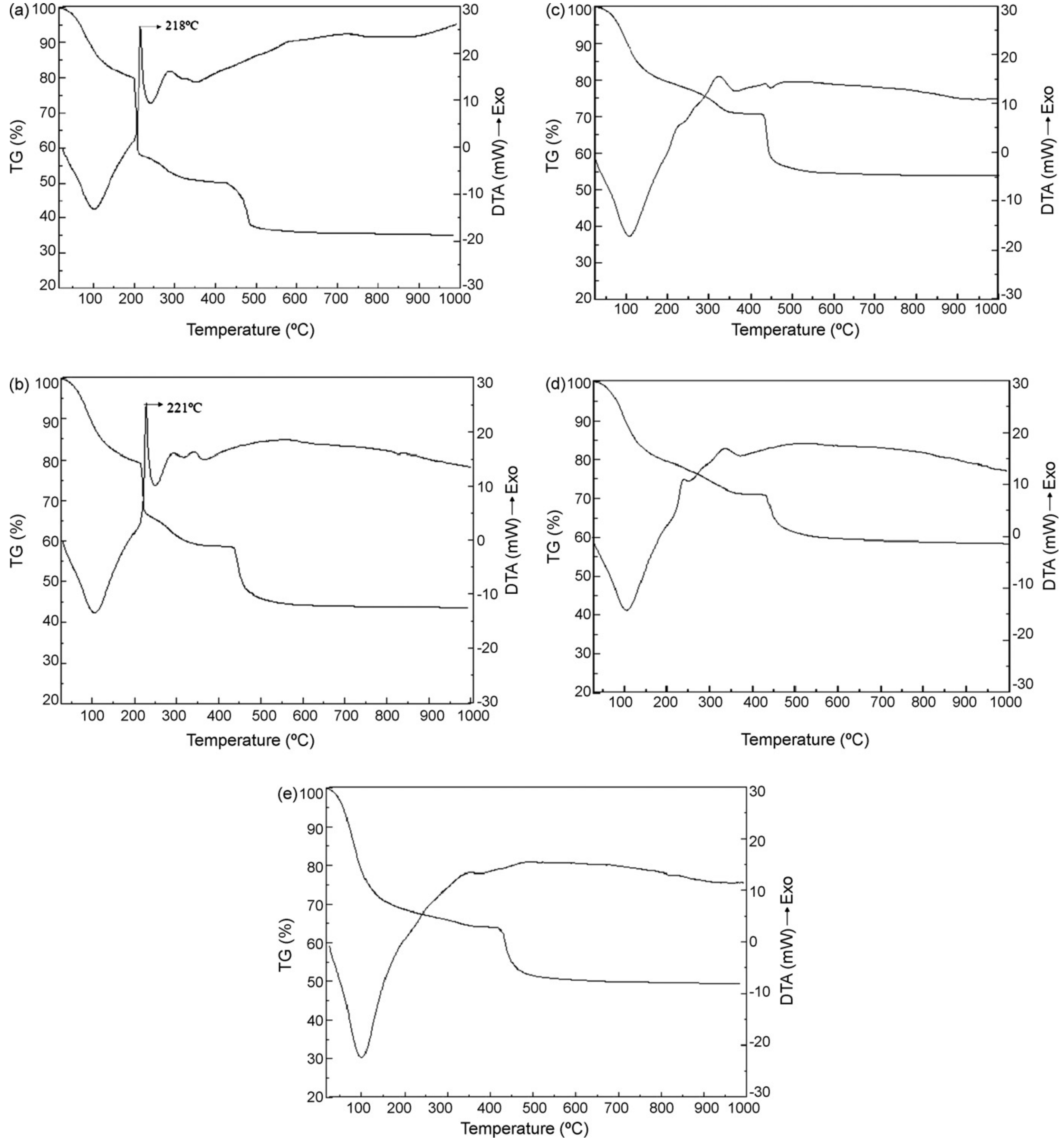

Fig. 6. TG/DTA curves of PAZ pretreated under special ambience at (a) 1 h; (b) 3 h; (c) 4.5 h; (d) 6 h and (e) 7.5 h.

posal was deduced that steam pretreatment had an extraordinarily significant effect on the thermal decomposition process of PAZ.

4. Conclusions

The steam pretreatment had an extraordinarily significant effect on the thermal decomposition mechanism of PAZ. The organic parts of PAZ were combusted in air flow and changed into H_2O and CO_2 and the displacement reactions were occurred between steam and the organic ligands. The inert (N_2) can improve the transformation from PAZ to ZrO_2. Therefore, different thermal behaviors of PAZ were deduced under different atmospheres.

Acknowledgements

The authors acknowledge the financial support of the National Natural Science Foundation (Grant Nos. 50672049, 60608010 and 50772059) and the Foundation for the Author of National Excellent Doctoral Dissertation of PR China (No. 200539).

References

[1] H.Y. Liu, X.Q. Hou, X.Q. Wang, Y.L. Wang, D. Xu, C. Wang, W. Du, M.K. Lü, D.R. Yuan, J. Am. Ceram. Soc. 87 (12) (2004) 2237.
[2] M. Pan, J.R. Liu, M.K. Lü, D. Xu, D.R. Yuan, D.R. Chen, P. Yang, Z.H. Yang, Thermochim. Acta 376 (1) (2001) 77.
[3] T. Gunji, H. Yamamoto, T. Hanaoka, K.K. Bnadoh, Y. Abe, Appl. Organomet. Chem. 14 (2000) 119.
[4] K. Chakadarty, M. Chatterjee, M.K. Naskar, B. Siladitya, D. Ganguli, J. Eur. Ceram. Soc. 21 (3) (2001) 355.
[5] M. Pan, J.R. Liu, F.Q. Fan, M.K. Lü, D.R. Yuan, D. Xu, J. Inorg. Mater. 16 (2001) 729.
[6] R.C. Pullar, M.D. Taylor, A.K. Bhattacharya, J. Inorg. Mater. 21 (1) (2001) 19.
[7] Y. Dzenis, Science 304 (5679) (2004) 1917.
[8] C.G.R. Nair, S. Mathew, K.N. Ninan, J. Thermal Anal. 37 (10) (1991) 2325.
[9] Y. Deutsch, Y. Natham, S. Sarig, J. Thermal Anal. 42 (1) (1994) 159.
[10] S.L. Ali, K. Majid, Thermochim. Acta 311 (1/2) (1998) 173.
[11] N. Petrova, D. Todorovsky, Mater. Res. Bull. 41 (3) (2006) 576.
[12] J.P. Zhao, W.H. Fan, D. Wu, Y.H. Sun, J. Non-Cryst. Solids 261 (1–3) (2000) 15.
[13] S.M. Dutt, R.L. Frost, J.M. Bell, AIP Conference Proceedings, vol. 430, 1998, p. 674 (Fourier Transform Spectroscopy).
[14] R.L. Frost, S.M. Dutt, J. Colloid Int. Sci. 198 (2) (1998) 330.
[15] Y. Abe, H. Tomioka, T. Gunji, Y. Nagao, T. Misono, J. Mater. Sci. Lett. 13 (13) (1994) 960.
[16] T. Gunji, H. Goto, Y. Kimata, Y. Nagao, T. Misono, Y. Abe, J. Polym. Sci. Polym. Chem. Ed. 30 (1992) 2295.