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Thermochimica Acta 246 (1994) 99–105

thermochimica
acta

Investigation on the mechanism of *n*-butanol interaction with zirconia powder

Lu Chang-Wei*, Qiu Hai-Bo, Feng Chu-De, Xi Tong-Geng,
Yang Xue-Hua, Chen Yun-Xian, Guo Jing-kun

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, 200050 Shanghai, People's Republic of China

Received 29 December 1993; accepted 7 April 1994

Abstract

The heterogeneous azeotropic distillation technique has been successfully applied to the preparation of ultra-fine sinterable zirconia powder having > 98% of the theoretical density at 1200°C. The mechanism of azeotropic distillation of *n*-butanol with a hydrous gel to prevent the formation of "hard" agglomerates has been investigated by TG–DTA–MS and FT-IR techniques.

Keywords: Agglomerate; Azeotropic; Butanol; Coupled technique; Distillation; Zirconia

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1. Introduction

Attention has been paid to the agglomerating state of zirconia powder by scholars and experts for many years [1,2]. Although the existence of agglomerates can increase the flow character of ultra-fine powders, it will cause the particles to accumulate poorly and make the green material defective or loosely compacted. The "hard" agglomerated state of particles is a key problem for the wet chemical preparation of ZrO_2 powder. In order to avoid the formation of a "hard" agglomerated state, one means which has been universally adopted is to wash the

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* Corresponding author.

SSDI 0040-6031(94)01829-6

powder with alcohol to remove water, so that the dehydration reaction Zr-OH + Zr-OH → Zr-O-Zr + H_2O of non-bridging hydroxyl groups on the surface of different particles during drying and ignition can be prevented; the formation of "hard" agglomerates is thereby avoided. Lee, Ready and co-workers [3,4] in addition to Kaliszewski and Heuer [5] studied the mechanism of interaction when alcohol was used to wash zirconia. The results of their research showed that the hydroxyl groups on the surface of zirconium hydroxide were replaced by ethoxy groups and the formation of "hard" agglomerates was prevented because the interactive chemical binding of non-bridging hydroxyls on the surface could not take place. The two neighbouring ethoxy groups react to form diethyl ether, which decomposes to $CH_2{=}CH_2$. These authors detected the absorption spectrum of $CH_2{=}CH_2$ gas by FT-IR spectrometry.

In this paper, *n*-butanol azeotropic distillation with hydrous gel has been used effectively to prevent the formation of "hard" agglomerates and to prepare powders with good sintering character. As a result, the sintering temperature for ultra-fine ZrO_2 was lowered appreciably to the region of 1200-1250°C. The mechanism of the interaction on the surface between *n*-butanol and $Zr(OH)_4$ colloid has been studied and certified experimentally by TG-DTA-MS and FT-IR techniques. The results show that, through *n*-butanol azeotropic distillation with $Zr(OH)_4$ colloid, the hydroxyl groups on the surface of the colloid are replaced by butoxy groups and the neighbouring two butoxy groups form butyl ether, which decomposes to form butene and water vapour. By using a quadrupole mass spectrometer, the positive ion mass spectra of $C_4H_8^+$ ($m/z = 56$) in the gases evolved in process of heating the processed colloid particles have been obtained.

2. Experimental

2.1. Sample preparation

By means of a routine aqueous ammonia method, $ZrOCl_2 \cdot Y(NO_3)_3 \cdot 6H_2O$ (3 mol% Y_2O_3) was prepared and then titrated against ammonium hydroxide solution to produce a precipitate. The Cl^- ions were rinsed out with deionized water. The resulting colloid was separated by centrifuging and dehydrated by azeotropic distillation with *n*-butanol, then dried in an oven at $< 110°C$. Finally, a very loose powder was obtained.

2.2. TG-DTA-MS analysis

The instruments used were an STA-429 simultaneous thermal analyzer (Netzsch Co., Germany) coupled with a QMG-511 quadrupole mass spectrometer (Balzers Co., Switzerland). The sample weight was 50 mg. The full scale for TG was 25 mg and that for DTA was 0.2 mV. The gas used was static Ar. The heating rate was 20°C min^{-1} over the range 20-1000°C. Parameters for MS were: mass scan speed 1 s amu^{-1}; mass filtering time 0.03 s. A Faraday cup was used to record the ion current signals. The proposed mass numbers, ion intensity and amplification were (respectively): H_2O^+ ($m/z = 18$), 10^{-11} A, × 1; CO_2^+ ($m/z = 44$), 10^{-11} A, × 1; $C_4H_8^+$ ($m/z = 56$), 10^{-11} A, × 10; $C_4H_{10}O^+$ ($m/z = 74$), 10^{-11} A, × 1; $C_8H_{18}O^+$ ($m/z = 130$), 10^{-11} A, × 1. The symbol P denotes the pressure in the MS analyser, and the symbol T denotes the temperature of the system.

2.3. FT-IR examination with temperature programming

A DWP-702 temperature programming instrument and a Nicolet FT-IR 5DX infrared spectrometer were used. Samples were prepared in the form of pressed KBr discs. The FT-IR spectra were recorded at 100, 200, 300 and 380°C under vacuum conditions.

3. Results and discussion

3.1. FT-IR spectra

The FT-IR spectra with programmed increase of temperature under vacuum (room temperature, 100°C, 200°C, 300°C and 380°C) for unprocessed $Zr(OH)_4$ (A) and for $Zr(OH)_4$ colloid processed with *n*-butanol (B) are shown in Fig. 1. The region 3800–3000 cm^{-1} in (A) shows the broad overlapping peaks of the different hydroxyl groups (including the molecular state of water). The peak at 1626 cm^{-1} indicates vibrational absorption arising from water of adsorption and of coordination; with increase in temperature, this peak rapidly became weaker and disappeared completely at 200°C. The peak at 1544 cm^{-1} corresponds to the vibrational absorption from the bridging hydroxyl groups. There is an obvious difference between (B) and (A), as can be seen from the C–O stretching vibration peaks of $-O-CH_2-(CH_2)_2CH_3$ at 1105 cm^{-1} and 1050 cm^{-1} (a) and the C–H stretching vibrations near 2900 cm^{-1} (b). The C–O stretching vibration peaks are clearly seen at 300°C. The C–H stretching peak is still evident at 375°C. These results illustrate that the *n*-butanol molecule remains in a state of strong chemical adsorption on the surface of the colloid particles.

3.2. TG–DTA–MS results

There is a large step in the TG curve from 118 to 600°C (Fig. 2) corresponding to a weight loss of $\approx 20\%$. There is a broad endothermic peak in the DTA curve at 130°C (Fig. 2), and the peak at 475°C shows the phase transition of $Zr(OH)_4$ from amorphous to tetragonal. Fig. 3 shows discrete CO_2^+ ($m/z = 44$) peaks at 130, 193 and 500°C. The $C_4H_8^+$ ($m/z = 56$) peak appears at 400°C, but there is no $C_4H_{10}O^+$ ($m/z = 74$) or $C_8H_{18}O^+$ ($m/z = 130$) peak. Fig. 4 shows the H_2O^+ ($m/z = 18$) mass spectrum which was obtained after the partial pressure of water in the vacuum system was reduced by introducing liquid nitrogen. A broad H_2O^+ peak related to the process of dehydration at 50–300°C and a CO_2^+ peak showing

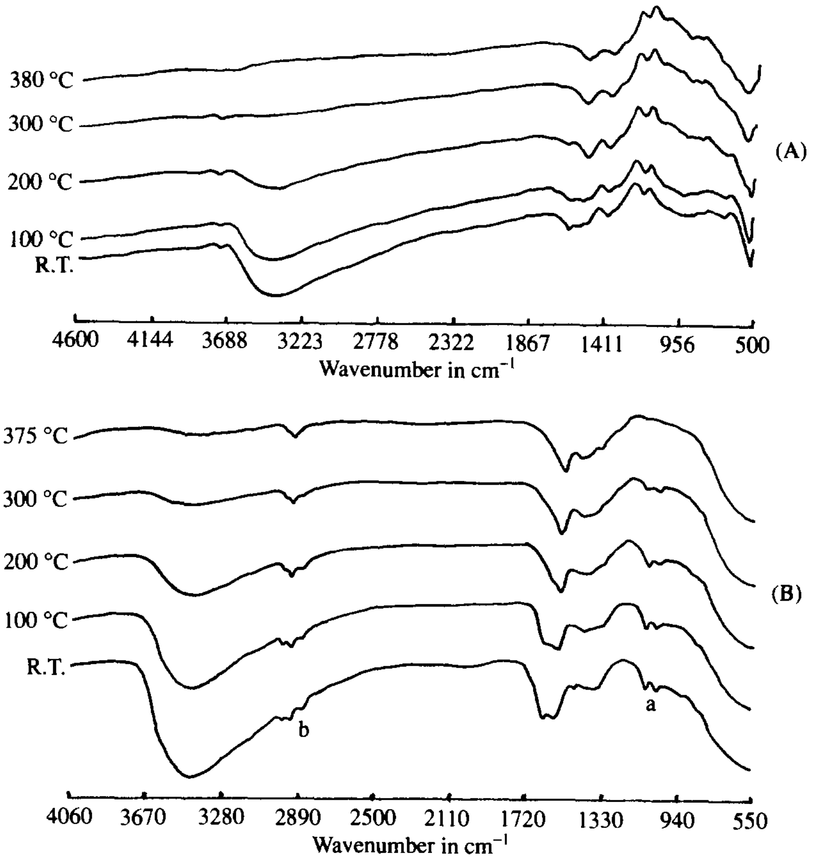

Fig. 1. FT-IR spectrum during programmed heating under vacuum for (A) unprocessed $Zr(OH)_4$ and (B) $Zr(OH)_4$ colloid processed with *n*-butanol.

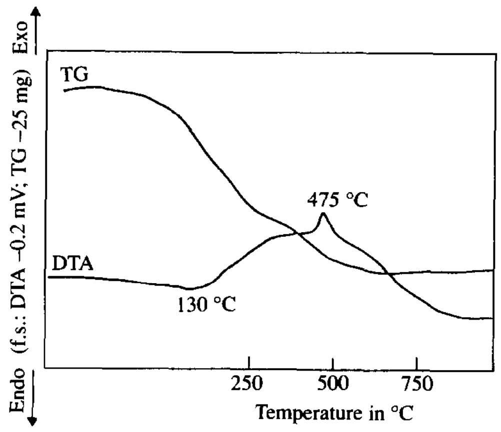

Fig. 2. DTA–TG curve of processed powder.

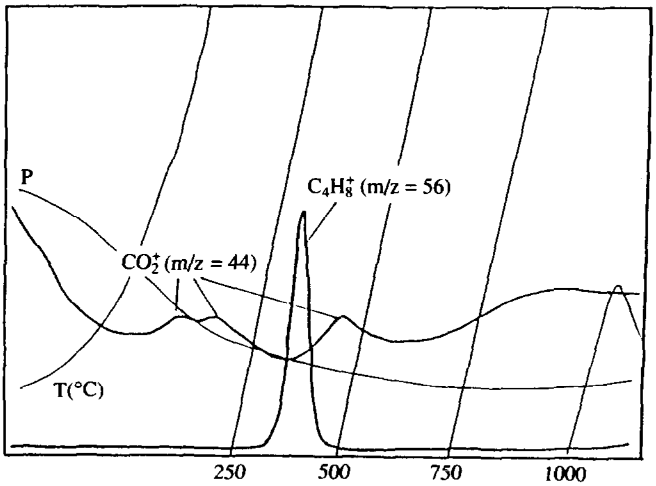

Fig. 3. Mass spectra of the processed powder (liquid N_2 was not used in the mass spectrometer for cold trapping).

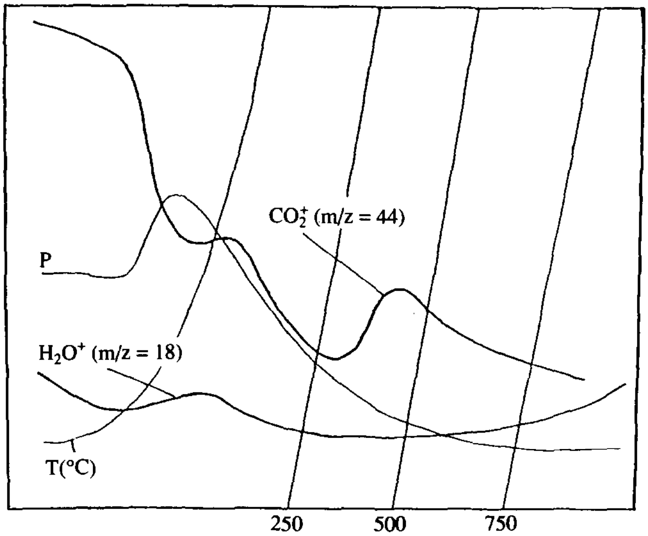

Fig. 4. Mass spectra of the processed powder (with use of liquid N_2).

the evolution of CO_2 gas can be observed. However, the reason for the absence of a $C_4H_8^+$ peak in Fig. 4 requires further study. All the results of TG–DTA–MS and FT-IR analyses suggest that the weight loss in the TG curve below 300°C is caused by the loss of physisorbed water and CO_2 from the surface of zirconium hydroxide colloid. The corresponding DTA curve shows an endothermic peak at 130°C and

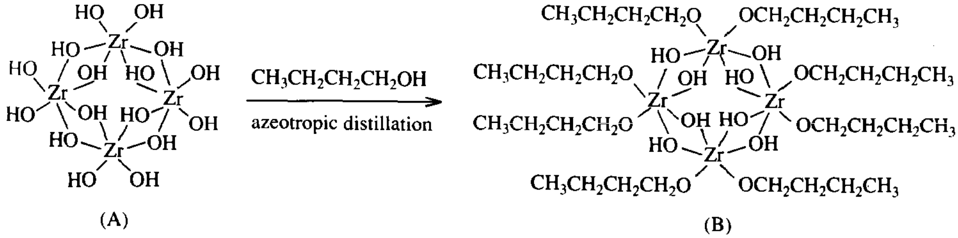

Fig. 5. Proposed structure of $Zr(OH)_4$ colloid treated by azeotropic distillation with *n*-butanol: (A) structure of $Zr(OH)_4$ determined by Zaitsev [6]; (B) structure proposed in the present work.

the mass spectrum shows peaks for CO_2^+ ($m/z = 44$) at 130 and 193°C as well as a broad peak for H_2O^+ ($m/z = 18$) between 50 and 300°C. There is a significant weight loss corresponding to an exotherm in the DTA curve at 475°C and the evolution of C_4H_8 (gas) and CO_2 from decomposition in the process of thermolysis. Meanwhile, the mass spectrum shows a $C_4H_8^+$ ($m/z = 56$) peak at 400°C and a CO_2^+ ($m/z = 44$) peak at 500°C. Because ZrO_2 is a well known dehydration catalyst for alcohols [7], it is not surprising that the *n*-butene positive ion peak can be detected by MS during the heating process.

Based on the results of TG–DTA–MS and FT-IR spectrometry, the processes of interaction of particles on the surface of the zirconium hydroxide colloid are tentatively proposed: first, the azeotropic phase formed by the water of adsorption and coordination of the colloid particles with *n*-butanol has been extracted strongly, so that the DTA curve shows only a small endothermic peak of dehydration at 130°C. The mass spectra in Fig. 3 show no H_2O^+ peak; a H_2O^+ peak is visible only when the background of H_2O^+ vapour has been reduced by adding liquid nitrogen (see Fig. 4). Then the non-bridging hydroxyls on the surface of zirconium hydroxide are replaced by butoxy groups during the azeotropic process. The results of IR spectroscopy show that the stretching vibrations of C–O and C–H are retained above 300°C. Based on all the results mentioned above, we propose a structure for $Zr(OH)_4$ colloid after azeotropic distillation with *n*-butanol (see Fig. 5, A and B). The studies show that the structure is consistent with the steric hindrance of the adsorbed butoxy groups on the surface of the particles. With increasing temperature, the particles are inhibited from approaching each other, and because of the catalytic action of ZrO_2 itself the two butoxy groups on the surface of the same particle react to form dibutyl ether, which quickly decomposes into two butene molecules and water. We can also see that, because of the azeotropic distillation of *n*-butanol and ZrO_2 powder, the water content of the processed colloid is very low, so that it is impossible to form chemical Zr–O–Zr bonds among the particles of zirconium hydroxide. As a result, the formation of "hard" agglomerates has been avoided.

4. Conclusion

Based on the results of TG–DTA–MS and FT-IR analysis, it is concluded that the azeotropic distillation of *n*-butanol with zirconia powder greatly inhibits the possibility of forming Zr–O–Zr bonds among the particles of zirconia from the water of adsorption and the non-bridging hydroxyl groups on the surface of the particles, so that the formation of "hard" agglomerates of powders can be avoided and the sintering properties of the processed powders are improved.

Acknowledgements

This work was supported by the foundations of Chinese National Natural Sciences and the State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences.

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