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ScienceDirect
Powder Technology 168 (2006) 59–63
POWDER TECHNOLOGY
www.elsevier.com/locate/powtec

Short communication

Tetragonal nanocrystalline zirconia powder with high surface area and mesoporous structure

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Received 19 December 2005; received in revised form 10 July 2006; accepted 13 July 2006
Available online 17 August 2006

Abstract

Nanocrystalline zirconia powder with high surface area, pure tetragonal phase and mesoporous structure was prepared by a surfactant-assisted route by using Pluronic P123 block copolymer as the surfactant. The zirconium to surfactant molar ratio, pH of precipitation, aging time and zirconium molarity were optimized by the Taguchi method of experimental design. The sample prepared under optimized conditions showed a high surface area of 175 m^2 g^{-1}, pure tetragonal crystallite phase and a mesoporous structure after calcination at 600 °C for 5 h. The X-ray diffraction and nitrogen adsorption analyses showed that the mesoporous structure and tetragonal phase were stable towards higher temperatures.

Keywords: Zirconia; Tetragonal phase; Surface area; Mesoporous structure

1. Introduction

Zirconia powder has become one of the industrially most important ceramic materials and also a potential third-generation catalyst support [1–4]. ZrO_2 has three polymorphs: monoclinic (m-phase, below 1170 °C), tetragonal (t-phase, between 1170 and 2370 °C) and cubic (c-phase, above 2370 °C) [4,5]. The high temperature cubic and tetragonal phases can be stabilized at room temperature by incorporating dopants in the lattice, e.g. CaO, MgO, Y_2O_3 and CeO_2 [6–8]. The tetragonal phase (t-ZrO_2), has both acidic and basic properties [9] and gives the most active catalyst for some catalytic reactions [10]. Another point is that the higher density of tetragonal vs. monoclinic ZrO_2 results in higher volume based activity for the tetragonal systems provided that the weight based activities are similar. However, the thermal stability of t-ZrO_2 is crucial since the transition of the tetragonal to the monoclinic phase results in sintering and deactivation of the catalyst. The use of zirconia powder requires a high specific surface area and suitable pore structure for catalysis applications. Therefore, more attention has been paid to the preparation of pure tetragonal zirconia with a high surface area in recent years. Many methods have been explored to get superfine ZrO_2 powders with high surface area and suitable pore size distribution such as glycothermal process [11], alcohothermal-SCFD (supercritical fluid drying) process [12,13], CO_2 supercritical drying [14,15], sol–gel method [16,17], solid-state reaction method [18], etc. Recently, much attention was paid to the synthesis of the nanostructured mesoporous oxides with high surface area and uniform pore size distribution using a surfactant-assisted route [19,20]. In this method there are several parameters, which significantly affect the surface area of the metal oxide, such as pH of precipitation,

Table 1
Parameters and their experimental levels

Parameter	Level 1	Level 2	Level 3
(A) Surfactant/Zr mol. ratio	0.05	0.03	0.01
(B) pH	11	10	9
(C) Aging time (h)	24	12	6
(D) Zr molarity (mM)	0.983	1.46	2.434

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doi:10.1016/j.powtec.2006.07.008

Table 2
Experimental conditions and BET area and tetragonal percent of the samples

Exp	Sample	Surfactant/Zr molar ratio	pH	Aging time (h)	Zr molarity	BET area (m^2 g^{-1})	Tetragonal (wt.%)	$\eta_{tetragonal\ phase}$	$\eta_{surface\ area}$
1	A-1	0.05	11	24	0.983	130	89	38.99	42.28
2	A-2	0.05	10	12	1.460	102.1	78	37.84	40.18
3	A-3	0.05	9	6	2.434	63.7	39	31.82	36.08
4	A-4	0.03	11	12	2.434	120	92	39.28	41.58
5	A-5	0.03	10	6	0.983	81	48	33.62	38.17
6	A-6	0.03	9	24	1.460	114	89	38.99	41.14
7	A-7	0.01	11	6	1.460	89	59	35.42	38.99
8	A-8	0.01	10	24	2.434	87	84	38.49	38.79
9	A-9	0.01	9	12	0.983	87.8	67	36.52	38.87

aging time, surfactant to metal molar ratio, etc. The Taguchi method, which is common in the design of industrial experiments, may be used for optimization of the process [21,22]. In this paper, the surfactant-assisted route by using Pluronic P123 block copolymer surfactant was used for the synthesis of nanocrystalline zirconia and the Taguchi method of experimental design was used to optimize the preparation conditions for the synthesis of zirconium oxide with high surface area and high content of the tetragonal phase.

2. Experimental

2.1. Zirconia powder preparation

In a typical preparation, aqueous ammonia (25 wt.%) was added dropwise at room temperature to an aqueous solution of zirconyl nitrate ($ZrO(NO_3)_2{\cdot}xH_2O$) and Pluronic P123 block copolymer surfactant under rapid stirring. After precipitation, the slurry was stirred for another 30 min and then refluxed at 84 °C under continuous stirring. After refluxing the mixture, it was cooled to room temperature, filtered and washed, first with deionized water and finally with acetone for an effective removal of the surfactant. The final product was dried at 110 °C for 24 h and calcined at different conditions. The zirconium to surfactant molar ratio, pH of precipitation, aging time and zirconium molarity were considered as the most important parameters for optimization of the precipitation conditions. Three levels of each parameter were used as shown in Table 1.

2.2. Characterization

The surface areas (BET) were determined by nitrogen adsorption at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. The XRD patterns were recorded on an X-ray diffractometer (Philips-PW-1840) using a Cu-K_α monochromatized radiation source. The amounts of tetragonal and monoclinic ZrO_2 present in the ZrO_2 samples and the crystallite sizes were estimated as reported elsewhere [18].

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out in air with a Netzsch STA 409 system in the temperature range between 25 and 900 °C at a heating rate of 10 °C/min. Infrared spectra were recorded on a NEXus Fourier transform infrared (FTIR) spectrophotometer using KBr pellets containing 1% weight sample in KBr.

3. Results and discussion

For optimization of the surface area and the tetragonal content, Taguchi design of L_9 orthogonal array was used to investigate the factors, such as surfactant/Zr ratio, pH, aging time and Zr molarity. The experimental conditions and the results are given in Table 2. All samples were calcined at 600 °C for 5 h.

As it can be seen, both the tetragonal weight percent and the specific surface area varied significantly with the preparation conditions. The changes in the tetragonal percent varied more

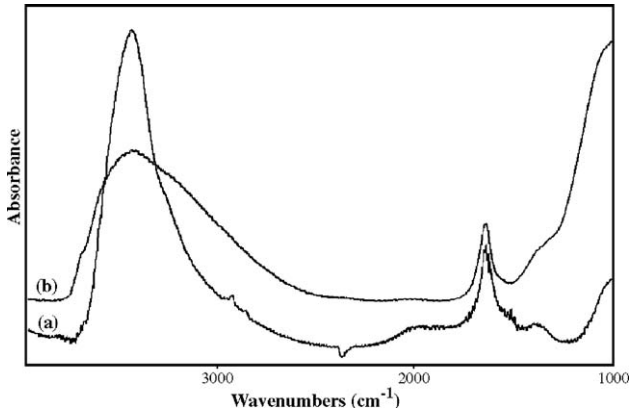

Fig. 1. IR spectra of the A-1 precursor, (a) after washing and (b) after heat treatment at 300 °C.

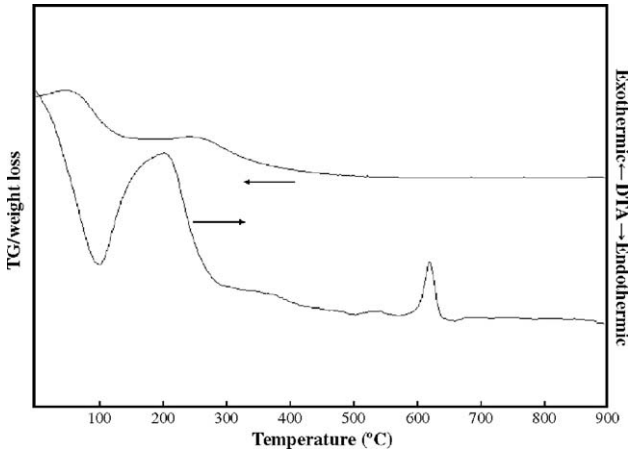

Fig. 2. DTA/TGA curves of the A-1 precursor.