## Solvothermal Synthesis of Spherical Zirconia Particles Having Meso-Macro Bimodal Pore Structures

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By the thermal reaction of tetrakis(acetylacetonato)zirconium in 1,4-butanediol at 300 °C for 2 h, spherical zirconia particles with large surface areas and large pore volumes both in the meso and macro pore regions were directly obtained. The thermal reactions at lower temperatures afforded intermediate compounds having a layered-structure, attributed to the formation of the unique pore system of the products obtained in 1,4butanediol.

Keywords: ZrO<sub>2</sub> | Solvothermal method | Bimodal pore structure

Zirconias and zirconia-based oxides have been used as catalysts and catalyst supports for various reactions,1-5 and control of the pore structure of these materials is greatly important. Besides catalytic applications, zirconias have been also attracting much attention as stationary phase supports for liquid chromatography,<sup>6-8</sup> and synthesis of spherical zirconia particles with homogeneous size and shapes has been investigated.<sup>9,10</sup> Sol-gel method is known as a preferable method for this purpose; however, the obtained products are amorphous or oxides with low crystallinity, and therefore, heat treatments are necessary to obtain well-crystallized products.11,12 Preparation of aerogel crystalline ziconias with large surface area and controlled pore structures via sol-gel process and subsequent supercritical drying has been also reported.<sup>13,14</sup> On the contrary, Inoue et al. previously reported that microcrystalline zirconias with high surface areas were directly obtained by the solvothermal method using several zirconium sources and organic solvents.<sup>15</sup> Influence of synthesis conditions, such as concentration of zirconium(IV)*n*-propoxide (ZNP) as the Zr source and reaction temperature, on the physical properties of the zirconia powders were examined using 1,4-butanediol (1,4-BG) and 1,5-pentanediol, and it was found that spherical zirconia particles with a large specific surface area and large pore volume in the mesopore region were directly obtained in 1,4-BG.<sup>16</sup> However, the pore sizes of the thus-obtained products were relatively small (<10 nm), and an expansion of the pore size distribution has been sought to improve their performance. In this study, solvothermal syntheses of zirconias in 1,4-BG were examined using tetrakis(acetylacetonato)zirconium ( $Zr(acac)_4$ ) and the pore structures of the products were investigated. Furthermore, to elucidate the reasons for the difference of the pore structures of these products, thermal treatments at low temperatures were conducted.

In a test tube, appropriate amounts of  $Zr(acac)_4$  and 1,4-BG (10, 20, or 40 mmol of  $Zr(acac)_4$  in 100 mL of 1,4-BG, or 48 mmol of  $Zr(acac)_4$  in 80 mL of 1,4-BG) were added and the mixture was set in a 300-mL autoclave. Into the gap between the test tube and the autoclave wall, 30 mL of 1,4-BG was poured additionally. After the atmosphere inside the autoclave was

replaced with nitrogen, the mixture was heated to 300 °C at a rate of 2.5 °C/min, and kept at that temperature for 2 h. After the solvothermal reaction for 2 h, the valve of the autoclave was slightly opened to remove organic vapor from the autoclave by flashing evaporation while keeping the temperature at 300 °C. After cooling, dry powders were obtained directly. The obtained products were calcined at 500 °C for 1 h in a box furnace. For comparison, synthesis of zirconias was also carried out using ZNP (10, 20, or 60 mmol in 100 mL 1,4-BG). To examine the formation process of the pore system, the Zr sources in 1,4-BG were also heated at lower temperatures, and the products were recovered by centrifugation, washed with acetone repeatedly, and then air-dried overnight.

The thus-obtained products and those calcined at 500 °C were characterized by several methods. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku RINT 2200VF using CuK $\alpha$  radiation. Scanning electron microscopy (SEM) measurements were performed on a JEOL JSM-6510AS. Nitrogen adsorption experiments were carried out with a Quantachrome Instruments NOVA 2200e for the samples calcined at 500 °C. Specific surface areas were calculated using the BET multipoint method and pore size distributions were calculated on the basis of N<sub>2</sub> adsorption isotherms using the BJH method.

Figure 1 shows XRD patterns of as-synthesized products obtained by the solvothermal treatment of ZNP or Zr(acac)<sub>4</sub> in 1,4-BG at 300 °C and the samples after calcination at 500 °C. For the product obtained from 10 mmol of ZNP in 100 mL of 1,4-BG, diffraction peaks solely for the tetragonal zirconia were observed. The crystallite size of the product calculated from the half-height width of the XRD peak was ca. 5 nm, which is in good agreement with the crystallite sizes reported in the previous study.<sup>16</sup> For the product synthesized from 60 mmol of ZNP in 1,4-BG, large peaks for the tetragonal phase and small peaks for the monoclinic zirconia were observed. After the calcination at 500 °C, phase transformation to the monoclinic ZrO<sub>2</sub> was observed. In the case of Zr(acac)<sub>4</sub>, the product obtained from 10 mmol of Zr(acac)<sub>4</sub> in 1,4-BG also showed diffraction peaks only for the tetragonal phase, which is consistent with the previous result.<sup>15</sup> On the contrary, small peaks for the monoclinic zirconia were observed for the product obtained from the 20 mmol Zr(acac)<sub>4</sub> solution, and the monoclinic zirconia phase was mainly observed for the product from the 48 mmol Zr(acac)<sub>4</sub> in 80 mL 1,4-BG solution, which suggests the products using Zr(acac)<sub>4</sub> were formed via an altered crystallization process.

In Figure 2, SEM images of the products are depicted. In the case of using ZNP, spherical particles were observed regardless of the ZNP concentration. The particle size of the product obtained from the 10 mmol ZNP solution was some hundred nanometers (a), and the particle size increased significantly as the amount of ZNP in 1,4-BG increased to 20 and 60 mmol



Figure 1. XRD patterns of the products obtained by the solvothermal treatment of ZNP or  $Zr(acac)_4$  in 1,4-BG at 300 °C and the samples after calcination in air at 500 °C. \*48 mmol  $Zr(acac)_4$  in 80 mL of 1,4-BG.

(b, c). On the other hand, the products obtained from the 10 mmol  $Zr(acac)_4$  solution were spherical particles with particle size of *ca*.  $1-2 \mu m$  (d), which were much larger compared with the product from the 10 mmol ZNP solution (a). The products from the 20 mmol  $Zr(acac)_4$  solution were mainly spherical particles with diameters of *ca*.  $3 \mu m$  and small particles were also observed (e). On the contrary, the products from the 48 mmol  $Zr(acac)_4$  in 80 mL 1,4-BG solution were composed of aggregation of fine particles and no spherical particles were observed (f).

In Figure 3, the  $N_2$  adsorption isotherms of the  $ZrO_2$  samples synthesized using ZNP are shown. The effect of the calcination temperature on the pore structure is shown in Figure S1. The sample from the 60 mmol solution had mesopores in the range of 2–10 nm; however, for those from the lower concentrations, the samples had much smaller pore volumes.



**Figure 2.** SEM images of the products ZNP or  $Zr(acac)_4$  in 1,4-BG by the solvothermal treatment at 300 °C; 10 (a), 20 (b), and 60 mmol (c) of ZNP; 10 (d) and 20 mmol (e) of  $Zr(acac)_4$  in 100 mL of 1,4-BG, and 48 mmol of  $Zr(acac)_4$  in 80 mL of 1,4-BG (f).

Figure 4 shows the N<sub>2</sub> adsorption isotherms for the ZrO<sub>2</sub> samples synthesized using  $Zr(acac)_4$ . The  $ZrO_2$  samples obtained by using Zr(acac)<sub>4</sub> had much larger pore volumes. The pore size distribution of the ZrO<sub>2</sub> sample obtained from the 10 mmol Zr(acac)<sub>4</sub> solution had a noticeable peak in the mesopore region of 2-10 nm. Quite interestingly, the pore size distribution of the sample obtained from the 20 mmol Zr(acac)<sub>4</sub> solution had two peaks, one at around 7 nm and the other at around 50 nm. The pore size distribution of the sample from the 40 mmol Zr(acac)<sub>4</sub> solution also showed two peaks (Figure S2). For the sample from the 48 mmol Zr(acac)<sub>4</sub> in 80 mL 1,4-BG solution, however, a broad pore size distribution from the mesopore to macropore region was obtained. The physical properties of the samples calcined at 500 °C are summarized in Table 1. The sample obtained from the 60 mmol ZNP solution had a large surface area of  $111 \text{ m}^2/\text{g}$  and a pore volume of  $0.16 \text{ cm}^3/\text{g}$ . However, for those obtained from the 10 and 20 mmol ZNP solutions, the BET surface areas and pore volumes decreased significantly. On the contrary, using the  $Zr(acac)_4$  solutions, the  $ZrO_2$  samples with large BET surface areas were obtained. In addition, these samples had much larger pore volumes compared with those obtained using ZNP. These results also suggest the texture of the



**Figure 3.** N<sub>2</sub> adsorption isotherm (a), pore size distribution (b), and V t plot (c) of the ZrO<sub>2</sub> samples obtained by heating ZNP in 1,4-BG at 300 °C, followed by calcination in air at 500 °C;  $\bullet$ ,  $\bigcirc$ : 10 mmol,  $\blacklozenge$ ,  $\diamondsuit$ : 20 mmol, and  $\blacksquare$ ,  $\square$ : 60 mmol, closed symbols: adsorption, open symbols: desorption.



**Figure 4.** N<sub>2</sub> adsorption isotherm (a), pore size distribution (b), and *V*-*t* plot (c) of the ZrO<sub>2</sub> samples obtained by heating Zr(acac)<sub>4</sub> in 1,4-BG at 300 °C followed by calcination in air at 500 °C;  $\bullet$ ,  $\bigcirc$ : 10 mmol and  $\bullet$ ,  $\diamond$ : 20 mmol in 100 mL of 1,4-BG, and  $\blacksquare$ ,  $\Box$ : 48 mmol of Zr(acac)<sub>4</sub> in 80 mL of 1,4-BG, closed symbols: adsorption, open symbols: desorption.

 Table 1. Physical properties of the zirconia samples synthesized by the solvothermal method

Zr source	(mmol)	1,4-BG	Surface area (m <sup>2</sup> /g)		Pore volume (cm <sup>3</sup> /g)	
		(IIIL)	BET	External*	Total	Mesopore*
ZNP	10	100	10.8		0.05	
	20	100	13.4	6.1	0.02	0.01
	60	100	111	4.9	0.16	0.15
$Zr(acac)_4$	10	100	101	13.2	0.13	0.10
	20	100	122	54.7	0.34	0.21
	48	80	114		0.35	

\*Calculated from the V-t plot.

products using  $Zr(acac)_4$  and ZNP were formed via slightly different processes.

To investigate the formation mechanism of the pore system. the solvothermal treatments of ZNP or Zr(acac)<sub>4</sub> in 1,4-BG were carried out at lower temperatures. When the mixture of 20 mmol ZNP in 100 mL of 1,4-BG was heated in a glass vessel, it became a transparent solution at ca. 140 °C, and then white precipitates were formed at ca. 160 °C (Figure S3(a)). For the 60 mmol ZNP solution, a yellow transparent solution was obtained at ca. 90 °C and precipitates were formed at ca. 160 °C (Figure S3(b)). In the case of the 20 mmol Zr(acac)<sub>4</sub> in 1,4-BG, a transparent solution was obtained at ca. 125 °C, and white precipitates were also formed at ca. 170 °C (Figure S3(c)). On the contrary, in the case of the 48 mmol Zr(acac)<sub>4</sub> solution, no precipitations were formed up to 190 °C (Figure S3(d)). In Figure 5, the XRD patterns of the precipitates obtained by the solvothermal treatments of ZNP and Zr(acac)<sub>4</sub> at 200 and 250 °C are shown. The product obtained by heating the 60 mmol of ZNP solution at 200 °C showed two sharp diffraction peaks at 7.40° and 8.48°, which correspond to lattice spacings of 11.9 and 10.4 Å, respectively. When the same solution was heated at 250 °C, similar peaks were observed. Thermal analysis revealed that the products contained considerably large amounts of organic moieties (Figure S4). From these results, we speculate the products obtained at lower temperatures have a layered-structure as shown in Figure 6. For the solvothermal reactions of metal alkoxides in 1,4-BG, the thermal reactions are presumed to proceed via a replacement of alkoxide groups with 1,4-BG to form glycoxide intermediates and a subsequent heterolytic cleavage of the O-C bonds of the glycoxides to form tetrahydrofuran (THF).<sup>17,18</sup> In the case of ZNP, similar reactions plausibly take place at the early stage of the reaction; however, as shown in Figure 5, intermediates having layered-structures were formed, suggesting the crystallization into ZrO<sub>2</sub> nanocrystals proceeded in a stepwise fashion. As mentioned above, in the case of the thermal treatments of ZNP in 1,4-BG at 300 °C, spherical particles were directly obtained. For the formation of products having such a spherical morphology, a droplet formation process would be indispensable. We suppose that the layered compounds melt to form droplets at elevated temperatures, and the crystallization to ZrO<sub>2</sub> nanocrystals takes place in the droplets with releasing THF molecules. For the products obtained from the 20 mmol Zr(acac)<sub>4</sub> solution, two sharp peaks were also observed at 7.02° and 8.08°. These peaks correspond to the lattice spacings of 12.6 and 10.9 Å, and these values are slightly larger than those of the products obtained from the 20 and 60 mmol ZNP solutions. In addition, shoulder peaks were recognized for the product from the Zr(acac)<sub>4</sub> solution. These results suggest that the layered structure obtained from the Zr(acac)<sub>4</sub> solution was slightly expanded and partly disordered. When the 20 mmol Zr(acac)<sub>4</sub> solution was heated at 250 °C, the product showed no peaks for the layered compound but the tetragonal ZrO<sub>2</sub>, indicating the layered structure is not stable enough at this temperature. These changes in the intermediates affect the texture of the products and hence spherical particles having meso and macro bimodal pore structure were attained.

In summary, by heating a 1,4-BG solution containing 20 mmol of  $Zr(acac)_4$  at 300 °C for 2 h, spherical  $ZrO_2$  particles with mesopores and macropores were directly obtained. By heating the  $Zr(acac)_4$  solution at 200 °C, an intermediate with a layered-structure was obtained. The intermediate compound had slightly larger lattice spacings and lower stability compared with those obtained by the thermal treatment of ZNP in 1,4-BG at 200 °C. These changes affect the reactivity of the intermediates and the pore structure of the spherical products composed of nanocrystalline zirconias. Using the obtained  $ZrO_2$  particles, superior properties in various applications, especially in catalysis and chromatography, are expected.



Figure 5. XRD patterns of the products obtained by heating 60 mmol ZNP (a) and 20 mmol  $Zr(acac)_4$  (b) in 100 mL 1,4-BG at 200 and 250 °C.



**Figure 6.** A predicted structure of the product obtained by the thermal reaction of ZNP in 1,4-BG at lower temperatures.

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Supporting Information is available on https://doi.org/10.1246/cl.200038.

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