

A Simple Alcohothermal Synthetic Route to High Surface Area Zirconia Aerogel

Juncheng Hu, Yong Cao, and Jingfa Deng*

Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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A novel alcohothermal process has been successfully developed to prepare the thermally stable tetragonal zirconia aerogel using a cheap inorganic salt as the starting material. The results showed that the as-prepared zirconia aerogel has a high surface area and a well-developed textural mesoporosity, which is highly attractive for potential applications in heterogeneous catalysis.

Zirconia is a technologically important material that has recently attracted considerable interest in a wide range of practical applications.¹ It is a unique material of excellent thermal stability and chemical inertness, moreover, its surface has both oxidizing and reducing properties, as well as acidic and basic properties.^{2,3} In heterogeneous catalysis, zirconia has been extensively studied as a promising candidate for catalysts and support material.³ In most cases, it is often desirable to have the zirconia material with a high accessible specific area as well as a large and well developed porous texture. Unfortunately, zirconia generally has surface areas of 100 m²g⁻¹ or less, which is rather small compared to the typical silica or alumina supports or catalysts. Higher surface areas are attainable with amorphous zirconia, but this was usually achieved at the expense of lower thermal stability.

Much effort has been devoted to the synthesis of thermally stable zirconias having a large surface area.⁴⁻⁶ The normal procedure usually consists of the calcination of a hydroxylated gel prepared by hydrolysis of zirconium salts in various mediums. One well-known approach that affords the formation of zirconia with a large surface area is the sol-gel method, where the zirconium alkoxides were routinely utilized as the starting materials.⁷ More recently, several surfactant-assisted approaches have also been developed to synthesize mesoporous zirconia with hexagonal pore structure.^{8,9} However, the preparation procedures for both processes are elaborate and time consuming. Moreover, the use of the highly expensive zirconium alkoxides or the surfactants is required, which strongly limits the possible production of zirconia with desirable features at a large scale. The development of a more convenient and economical methodology to prepare catalytically attractive zirconia material from simple zirconium salts is essentially needed.

Solvothermal process has been shown to be a powerful technique for generating novel materials with interesting properties.¹⁰ In the present letter, we report a novel alcohothermal-supercritical fluid drying (alcohothermal-SCFD) process for the preparation of a large surface area zirconia aerogel using a cheap inorganic salt (Zr(NO₃)₄·5H₂O) as starting material. This novel synthesis route affords the preparation of the zirconia aerogel with several desirable features including a large surface area as well as pore volume and a well-developed porosity in the mesoporous range, providing a new economical approach for the production of large surface area zirconia aerogel.

The novel procedure consists of two consecutive synthetic

steps involving the alcohothermal process followed by the supercritical fluid drying (SCFD) treatment. Briefly, appropriate amounts of Zr(NO₃)₄·5H₂O were dissolved in 50 mL absolute ethanol to obtain a 0.3 mol·L⁻¹ solution followed by putting the solution into an autoclave of 50 mL capacity. After sealed, the autoclave was maintained at 383 K for 60 min, and then allowed to cool to room temperature. A translucent alcohothermal gel was thus obtained. The ethanol gel was aged at room temperature for 180 min. The gel was finally allowed a supercritical fluid drying process (the second stage) to obtain the aerogel samples. Calcination of the SCF dried sample was conducted in a muffle oven in the air for 120 min.

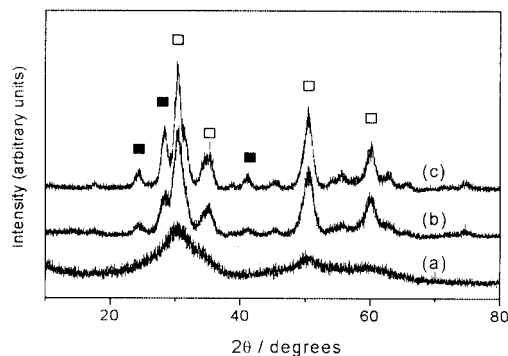
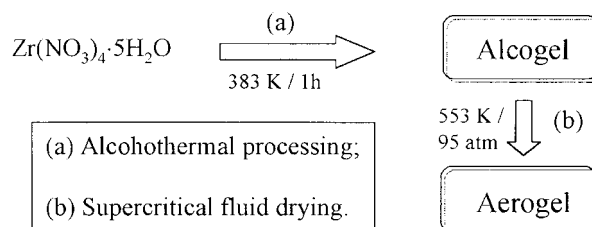


Figure 1. X-ray diffraction patterns of the nanocrystalline zirconia aerogel: (a) as-synthesized, (b) calcined at 673 K for 2 h, (c) calcined at 773 K for 2 h. (■): monoclinic phase, (□): tetragonal phase.

The samples were characterized by X-ray powder diffraction (XRD) method, operating on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range from 10–80°. Figure 1(a) shows the typical XRD patterns recorded for the zirconia aerogel derived by an alcohothermal-SCFD method. These broad diffraction patterns are characteristic of nanoparticles of tetragonal zirconia with a low crystallinity. The mean crystalline size of the zirconia aerogel, deduced from the full width at half-maximum, are reported in Table 1. The calculated mean crystalline size (D_{hkl}) for the as-synthesized aerogel sample was about 1.1 nm. After calcination at 673 K for 2 h, a sharpening

of the diffraction peaks for the zirconia sample was observed in Figure 1(b), reflecting a slightly crystallite growth of the zirconia sample. Moreover, several new weak diffraction bands corresponding to monoclinic phase were also observed in Figure 1(b), suggesting the occurring of a slight transformation of the tetragonal to monoclinic phase in the 673 K calcined sample. Further calcination of the sample at 773 K results in progressively sharpening of the diffraction peaks corresponding to two phases, indicating the further enlargement of the crystallite size with the increase the calcination temperature.

To investigate the microstructures of the as-synthesized zirconia aerogel, transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Figure 2 shows the TEM image of the zirconia aerogel derived through an alcoholthermal-SCFD route. It can be seen that the as-prepared zirconia sample is highly porous in nature, which consists of clusters of cross-linked particles smaller than 2 nm. This observation is in good agreement with the result obtained from XRD.

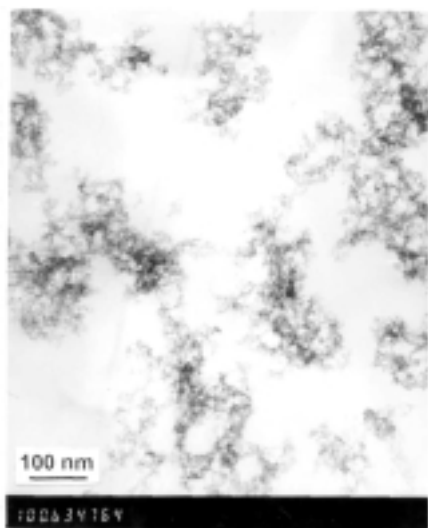


Figure 2. TEM microscopy of the as-prepared zirconia aerogel.

The surface area of the samples was measured using the BET method by N_2 adsorption and desorption at 77 K in a micromeritics ASAP2000 system. The surface area, pore volume and pore radius for the alcoholthermal-SCFD derived zirconia as well as the samples calcined at higher temperatures are compiled in Table 1. The pore size distribution measurements show that a well-developed mesostructure was achieved for the aerogel samples, which exhibiting a narrow pore size distribution in the range of 20–22 nm. The effect of the calcination temperature on surface area is dramatic as reported in the literature.¹¹ The temperature causes severe loss of surface area and pore volume, as seen in Table 1, as well as transformation in the structure of the sample, as demonstrated by XRD experiments. The as-synthesized zirconia sample has a large surface area and pore volume of up to $462 \text{ m}^2\text{g}^{-1}$ and $2.90 \text{ cm}^3\text{g}^{-1}$,

Table 1. Surface area and pore structure data of zirconia aerogel.

Sample	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$V/\text{cm}^3\cdot\text{g}^{-1}$ ^d	D/nm ^c	D_{hkl}/nm
ZrO_2^{a}	462	2.90	20.42	1.1
ZrO_2^{b}	270	0.89	21.71	2.0
ZrO_2^{c}	206	0.79	22.72	3.0

^aThe as-synthesized zirconia aerogel. ^bCalcined at 673 K for 2 h. ^cCalcined at 773 K for 2h. ^dBJH adsorption pore volume. ^eBJH adsorption average pore diameter.

respectively. Upon calcination at 673 K, the zirconia sample presents a surface area of $270 \text{ m}^2\text{g}^{-1}$ and a reduced pore volume of $0.89 \text{ cm}^3\text{g}^{-1}$. When calcination temperature goes to 773 K, the sample still retains a rather high surface area of $206 \text{ m}^2\text{g}^{-1}$.

It should be noted that the present alcoholthermal-SCFD derived zirconia aerogel is gray in color. The presence of adsorption bands around 3000 cm^{-1} in the IR spectra for the aerogel sample demonstrates the presence of ethoxy-moiety on the surface of the sample. After calcination in air at temperature above 673 K, a white colored sample can be readily obtained. Based on the IR measurements, only trace amount of carbonaceous residues was found to be present on the calcined sample. Therefore, the present synthetic method can allow the convenient preparation of pure zirconia materials for potential applications in heterogeneous catalysis.

In summary, we have successfully demonstrated a novel alcoholthermal-SCFD synthetic process for the preparation of thermally stable large surface area zirconia aerogel using a cheap inorganic salt as the starting material. The zirconia aerogel maintained a large surface area as well as the textural mesoporosity even after calcination at a high temperature of 773 K.

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References and Notes

- 1 K. Tanabe, M. Misono, Y. Ono, and H. Hattori, "New Solid Acids and Bases," Kodansha, Tokyo; Elsevier, Amsterdam, (1989).
- 2 T. Yamaguchi, *Catal. Today*, **20**, 199 (1994).
- 3 K. Tanabe, *Mater. Chem. Phys.*, **13**, 347 (1985).
- 4 P. D. L. Mercera, J. G. Van Ommen, E. B. M. Doesburg, A. J. Burggraaf, and J. R. H. Ross, *Appl. Catal.* **57**, 127 (1990).
- 5 Q. Sun, Y. Zhang, J. Deng, S. Chen, and D. Wu, *Appl. Catal.*, **152**, L165 (1997).
- 6 M. Inoue, K. Sato, T. Nakamura, and T. Inui, *Catal. Lett.*, **65**, 79 (2000).
- 7 J. B. Miller, S. E. Rankin, and E. I. Ko, *J. Catal.*, **148**, 673, (1994).
- 8 A. Kim, P. Bruinsma, Y. Chen, Li-Q Wang, and J. Liu, *Chem. Commun.*, **1997**, 161.
- 9 G. Pacheco, E. Zhao, A. Garcia, A. Sklyarov and J. J. Fripiat, *Chem. Commun.*, **1997**, 491.
- 10 Y. T. Qian, *Adv. Mater.*, **11**, 1101 (1999).
- 11 M. A. Aramendía, V. Boráú, C. Jiménez, J. M. Marinas, A. Marinas, A. Porras, and F. J. Urbano, *J. Catal.*, **183**, 240 (1999).