

Nanocrystalline Hydrous Zirconia from Zirconium Tungstate

Luciana M. Somavilla,^{‡,§} Janete E. Zorzi,^{†,‡} Giovanna Machado,[¶] Gustavo R. Ramos,[‡]

Cintia L. G. de Amorim,[‡] and Cláudio A. Perottoni^{‡,§}

[‡]Universidade de Caxias do Sul, 95070-560, Caxias do Sul, RS, Brazil

[§]PGCIMAT-Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre, RS, Brazil

[¶]Centro de Tecnologias Estratégicas do Nordeste—CETENE, 50740-540, Recife, PE, Brazil

Crystalline hydrous zirconia $(ZrO_2 \cdot 2H_2O)$ with volumeweighted average domain size of 1.5 nm was obtained by soaking zirconium tungstate (α -ZrW₂O₈) in boiling 1M NaOH solution for 5 h. The selected area electron diffraction pattern of hydrous zirconia particles could be indexed according to a tetragonal lattice with a = 1.463(4) Å and c = 2.535(6) Å. Upon heating to 60° C under a vacuum of 10^{-5} mbar, hydrous zirconia dehydrates reversibly. Further heating to 850° and 1000°C resulted in the formation of tetragonal and monoclinic zirconia, respectively. Some of the nanocrystalline hydrous zirconia produced from zirconium tungstate coalesced into transparent, nearly pore-free aggregates. The formation of these almost fully densified aggregates of hydrous zirconia, and the observed dehydration under very mild conditions, suggests that it could be possible to obtain transparent bodies of zirconia, with unprecedented small crystallite size, with the controlled deposition of the extremely small hydrous zirconia nanoparticles from a water-based suspension.

I. Introduction

ZIRCONIA (ZrO₂) is an outstanding ceramic material, with applications that span from high performance transformationtoughened structural engineering ceramics to catalysts, solid electrolytes, and oxygen sensors, to cite just a few.^{1–3} Such diverse applications rely on the unique properties of zirconia, which include high fracture toughness, relatively high hardness, wear resistance, low coefficient of friction, high melting point, good ionic conductivity, and low thermal conductivity.^{4–7}

Three polymorphs of zirconia are widely known which adopt monoclinic, tetragonal, and cubic crystalline structures.^{2,4,5} Other crystalline polymorphs of zirconia were obtained at high pressure and high temperature and also by fast cooling to liquid nitrogen temperature.^{3,8}

Many properties of nanocrystalline materials are fundamentally different from those of bulk materials. Some specific advantages of nanocrystalline ceramic materials include superior phase homogeneity and the possibility of low-temperature sintering.⁹ Besides structural applications, nanocrystalline ceramics have found application in areas such as electronics, optics, and catalysis.¹⁰ In fact, the reduced size of nanosized particulate materials, and the presence of edges and corners, often leads to an increased catalyst activity.^{11,12}

Zirconia has been used in heterogeneous catalysis both as a support for the catalyst as well as the catalyst in itself.^{6,13–15}

W.-C. Wei-contributing editor

Manuscript No. 28665. Received September 25, 2010; approved December 13, 2010. This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil). Because of the low concentration of Lewis acid sites, zirconia has found application as catalyst, for instance, in the isomerization of olefins and epoxides, dehydration of alcohols, and hydrogenation of olefins and carboxylic acids.^{11,12}

The surface area of zirconia powder is affected by the preparation conditions and is highly dependent on the precursors.⁶ Amorphous zirconia with specific surface area of $200-300 \text{ m}^2/\text{g}$ has been obtained by different methods.¹² Indeed, several different methods have been investigated as routes for the synthesis of nanometer-sized zirconia, including sol–gel process, spray pyrolysis, chemical precipitation, mechanochemical processing, gas-phase reaction, hydrothermal synthesis, and salt-assisted aerosol decomposition.^{1,2,6,7,16} Among these methods, aqueous precipitation of zirconium hydroxide or hydrous zirconia constitutes an interesting route for the preparation of precursors to make ultra fine zirconia powder.¹ Nanocrystalline tetragonal zirconia produced by some of these methods has been reported with mean crystallite size in the 2.9–6 nm range.^{2,17–21}

Zirconia produced from amorphous precursors (gel, precipitated, etc.) usually begin to crystallizes at around $400^{\circ}-600^{\circ}$ C.^{17,19–21} The amorphous precursors usually begin crystallizing into the metastable tetragonal phase, not the thermodynamically stable monoclinic phase. The tetragonal phase thus obtained can be retained at high temperatures. For instance, the crystallization of zirconia gel into the *t*-phase begins at 400°C and the $t \rightarrow m$ conversion occurs at 1000°C.^{19–22} The crystallization into the metastable *t*-ZrO₂ phase has been explained in terms of the similarity between the structures of the amorphous and the *t*-phase, crystallite size, and deformation effects, as well as the presence of ionic impurities.^{18,19–22} Recent results, however, suggest that nanocrystalline *t*-ZrO₂ is not just kinetically metastable, but can be truly thermodynamically more stable than monoclinic zirconia below 1200°C, as long as coarsening is precluded.¹⁸

Hydrous zirconia is very often found among the intermediate products in the preparation of nanocrystalline zirconia. Hydrous zirconia is also used as catalyst for the reduction of aldehydes and ketones and the oxidation of secondary alcohols with ketones.⁶

In this work, we report on the production of very small and narrow size distribution hydrous zirconia nanoparticles, starting from zirconium tungstate powder (ZrW2O8). The evolution of hydrous zirconia toward t-ZrO2 and m-ZrO2 was followed by successive thermal treatments. The product obtained from zirconium tungstate was characterized by transmission electron microscopy (TEM), scanning electronic microscopy (SEM), semiquantitative elemental analysis by energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and diffuse reflectance infrared Fouriertransform spectroscopy (DRIFTS). Selected area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy (HRTEM) images allowed to confirm the crystalline nature of the hydrous zirconia nanoparticles and also to determine their Bravais lattice and to estimate their lattice parameters.

[†]Author to whom correspondence should be addressed. e-mail: jezorzi@ucs.br

II. Experimental Procedure

(1) Sample Preparation

A white precipitate was obtained by soaking micrometer-sized zirconium tungstate (α -ZrW₂O₈) powder (Wah Chang, Albany, OR), with boiling NaOH 1*M* solution for 5 h, with magnetic stirring. The precipitate was washed with water several times, filtered (or centrifuged) and dried overnight in a oven at 120°C.²³ The white precipitate powder was characterized as obtained and after being submitted to successive 24 h thermal treatments in a tubular furnace, in air, at increasing temperatures from 500° up to 1300°C. Amorphous zirconium tungstate was prepared by pressing α -ZrW₂O₈ at 7.7 GPa for 15 min, following a procedure described previously.²⁴

(2) Materials Characterization

X-ray powder diffraction analysis at room temperature was performed with a XRD 6000 diffractometer (Shimadzu, Shimadzu Corp., Tokyo, Japan) using CuK α radiation ($\lambda = 0.15418$ nm), in the angular range from 5° to 80° (2 θ), with a step size of 0.05° and 2 s integration time. The diffractometer was equipped with Soller slits both in the primary and secondary beams, a 1° divergence slit, a 0.15 mm receiving slit, and a graphite monochromator in the secondary beam. Peak positions and intensities were determined by fitting a pseudo-Voigt peak profile to individual Bragg peaks using Winplotr software, taking into account CuK $\alpha_{1,2}$ contributions.²⁵ The volume-weighted average domain size was estimated from the integral width of individual Bragg peaks according to Young.²⁶ The instrumental contribution to the peak width was estimated using high-purity silicon powder (Shimadzu).

TGA was performed using a TGA-50 thermobalance (Shimadzu). Heating rate was 20°C/min and all the runs were carried out under a flow of 50 ml/min of high-purity nitrogen. DRIFTS analysis was performed on a Spectrum 400 spectrometer (Perkin-Elmer, Waltham, MA), using KBr as dispersant and 32 scans. The measurements were carried out with samples as obtained and after thermal treatment at 1300°C during 24 h.

SEM images and semiquantitative elemental analysis by EDS were carried out using a SSX-550 scanning electron microscope (Shimadzu) operating at 15 kV. Integral peak areas were used in the elemental semiquantitative analysis, in which matrix effects were corrected using the ZAF method.²⁷ For the SEM analysis, samples were coated either with carbon (SEM imaging) or gold thin films (EDS).

Individual nanoparticles were observed using a transmission electron microscope JEM2010 (JEOL, Tokyo, Japan) operating at 200 kV and equipped with an EDS system. Samples for TEM analysis were prepared by dispersion of the powder in isopropanol. A small amount of this suspension was dispersed on a holey carbon grid. Particle size distribution was determined from the analysis of TEM images showing well-defined individual nanoparticles. The crystalline nature of the hydrous zirconia was confirmed by HRTEM micrographs and SAED patterns. Indexing of the diffraction spots in the SAED patterns was performed on the basis of the corresponding interplanar distances as obtained with ProcessDiffraction.²⁸ Lattice parameters were calculated using XRDA.²⁹ Optical microscopy images of micrometer-sized aggregates were obtained with a Axioscope A₁ microscope (Carl Zeiss, Göttingen, Germany) in transmitted-light mode.

III. Results and Discussion

The X-ray powder diffraction pattern from the white precipitate obtained after soaking zirconium tungstate in boiling 1M NaOH solution is typical of an amorphous or nanocrystalline material (Fig. 1). EDS semiquantitative elemental analysis obtained by SEM (Fig. 2) revealed that the white precipitate is almost completely depleted of W, thus suggesting that soaking of α -ZrW₂O₈ in hot sodium hydroxide solution is a selective process in which part of the structure is leached. In fact, the



Fig. 1. X-ray powder diffraction patterns of (a) the white precipitate obtained after soaking zirconium tungstate in boiling 1*M* NaOH solution for 5 h and (b) pristine zirconium tungstate (α -ZrW₂O₈).

soaking of zirconium tungstate was accompanied by a 85% weight loss and, according to EDS semiquantitative elemental analysis, the tungsten content was reduced from 24%mol in zirconium tungstate to <0.6%mol in the white precipitate.

The selective leaching of tungsten by soaking of ZrW_2O_8 in boiling NaOH solution was further confirmed by chemical analysis of the filtered solution, which revealed the presence of the WO_4^{-2} ion by reacting it with hydrochloric acid and a small pellet of zinc, giving a blue coloration (tungsten blue).³⁰ A second test with tin chloride also confirmed the presence of the tungstate ion in solution.³⁰ Accordingly, the reaction taking place upon soaking of zirconium tungstate with sodium hydroxide solution should produce either hydrous zirconia

$$ZrW_2O_8 + 4NaOH \rightarrow ZrO_2 \cdot 2H_2O + 2Na_2WO_4$$

or anhydrous zirconium hydroxide

 $ZrW_2O_8 + 4NaOH \rightarrow Zr(OH)_4 + 2Na_2WO_4$

the latter probably getting some water from the solution to give $Zr(OH)_4 \cdot nH_2O$. After neutralizing the waste solution with HCl, tungsten can be recovered in the form of calcium tungstate by precipiting it with calcium chloride.



Fig. 2. Energy-dispersive spectroscopy analysis of (a) α -ZrW₂O₈ and (b) the white precipitate obtained from soaking zirconium tungstate in boiling NaOH solution



Fig. 3. TGA analysis of the white precipitate dried overnight in a oven at 120° C and them exposed to air before the measurement.

Zirconium hydroxide $Zr(OH)_4 \cdot nH_2O$ and hydrous zirconia $ZrO_2 \cdot nH_2O$ are structurally very similar and have been often treated as a single compound in the literature. In fact, according to the literature the probable structure of hydrous zirconia differs slightly from that of zirconium hydroxide, with Zr atoms bonded by an oxygen atom instead of a pair of hydroxo bridges.¹ Despite of the great similarity, there are some differences between hydrous zirconia and zirconium hydroxide that may help to clarify the nature of the white precipitate obtained from zirconium tungstate. For instance, zirconium hydroxide readily dissolves into hydrochloric acid 1*M* solution, while hydrous zirconia is relatively impervious to acid digestion.^{1,31}

The white precipitate obtained from ZrW₂O₈ resisted to treatment with hydrochloric acid 1M solution for ten minutes with a weight loss inferior to 9%.³¹ Moreover, upon heating, the white precipitate obtained by soaking zirconium tungstate in hot sodium hydroxide solution undergone a weight loss around 23%, as can be seen in Fig. 3. The weight loss upon heating is reported to be around 22% and 32% for hydrous zirconia and hydrated zirconium hydroxide (Zr(OH)₄ · 2H₂O), respectively.¹ The weight loss upon heating and the resistance to acid digestion both indicate that the white powder obtained by soaking zirconium tungstate in boiling NaOH solution is, at least, mainly composed of hydrous zirconia, $ZrO_2 \cdot 2H_2O$. Furthermore, the weight loss of the sample in the soaking process (about 85%, by measuring the weight of the dehydrated precipitate) is also consistent with the formation of hydrous zirconia (79% weight loss considering the dehydrated product), especially considering the losses during the process and that some zirconia may be well dissolving into the boiling NaOH solution. For comparison, the weight loss for the formation of anhydrous zirconium hydroxide should be of 74%.

Noteworthy, the 23% weight loss that the sample of hydrous zirconia exhibits upon heating to 600° C is also observed under very mild conditions, when the sample is submitted to a thermal treatment at 60° C, in a vacuum of 10^{-5} mbar during 5 h. Upon exposure to ambient conditions, samples of dehydrated hydrous zirconia absorb water until fully recovering its initial mass. Also, the precise weight loss exhibited by the samples of hydrous zirconia may vary according to the conditions under which the sample was storaged.

The presence of water in the white precipitate is also evident in the DRIFTS results (Fig. 4). Infrared bands assigned to O–H stretching and to the water scissoring mode, at around 3500 and 1640 cm⁻¹, respectively, are clearly seem in the DRIFTS spectrum of the white precipitate. These bands are absent (or are very weak) in the spectrum of the sample heated to $1300^{\circ}C/24$ h. Besides that, the DRIFTS spectrum of the white precipitate clearly exhibits an infrared band at 1340 cm⁻¹, which has been assigned to coordinated hydroxyl groups (δ Zr–O–H) in hydrous zirconia.³²



Fig. 4. DRIFTS analysis of (—) the white precipitate obtained by soaking of zirconium tungstate with sodium hydroxide solution (dried overnight in a oven at 120° C and them exposed to air before the measurement) and (- - -) m-ZrO₂ obtained from the white precipitate by thermal treatment at 1300° C/24 h.

The findings so far described strongly suggest that the white precipitate obtained by soaking zirconium tungstate with sodium hydroxide solution can be identified as mainly composed of hydrous zirconia, $ZrO_2 \cdot 2H_2O$. However, it is not possible to tell, solely on the basis of XRD analysis, whether the hydrous zirconia obtained from zirconium tungstate is truly amorphous or just nanocrystalline. TEM analysis was thus performed and some results are presented in Fig. 5.

TEM images show agglomerates of nanoparticles <2 nm. In fact, the nanoparticle size distribution histogram (inset on Fig. 5a) obtained from the analysis of TEM images reveals a monomodal distribution with an average diameter of 1.8 nm and a full-width at half-maximum of only 0.6 nm. Furthermore, the HRTEM image in Fig. 5(b) clearly exhibits crystalline planes, giving strong evidence that the hydrous zirconia nanoparticles are actually nanocrystalline instead of truly amorphous. This has been corroborated by the SAED pattern shown as an inset in Fig. 5(b), which exhibits well-defined diffraction spots. The SAED pattern was analyzed using ProcessDiffraction,²⁸ yielding a set of four interplanar distances (2.535, 1.465, 0.957, and 0.702 Å) which could be indexed according to a tetragonal Bravais lattice, as the (001), (100), (111), and (201) lattice planes, with a = 1.463(4) A and c = 2.535(6) A. The actual lattice parameters should vary according to the water content of the sample under the vacuum conditions during the TEM analysis.

The evolution of the sample of hydrous zirconia upon successive 24 h thermal treatments at increasing temperatures was followed by XRD. Figure 6 shows XRD patterns taken at ambient temperature for a hydrous zirconia sample as prepared, and after successive thermal treatments from 500° up to 1300°C.

The pristine sample exhibit broad peaks, characteristic of a material with very small coherent domain size. Those broad peaks remain almost unaltered even after prolonged thermal treatments up to 600°C. Coarsening begins at 600°C, but reasonably well-defined *t*-ZrO₂ Bragg peaks appear only after a 800°C/24 h thermal treatment. Bragg peaks from *m*-ZrO₂ became more evident in the pattern taken from the sample heated to 1000°C. The tetragonal and monoclinic phases of zirconia coexist in samples heated up to 1200°C. Above this temperature, only Bragg peaks from *m*-ZrO₂ are seen in the XRD pattern of the sample.

The high temperature needed to promote crystallization of nanocrystalline hydrous zirconia into t-ZrO₂ is noteworthy. Indeed, while amorphous precursors usually start to crystallize into t-ZrO₂ at temperatures between 400° and 600°C, the hydrous zirconia obtained by soaking zirconium tungstate with



Fig.5. (a) TEM image of hydrous zirconia nanoparticles. The inset shows the particle size distribution. (b) HRTEM image exhibiting individual hydrous zirconia nanoparticles with clearly distinct crystalline planes. The inset shows the SAED pattern of hydrous zirconia nanoparticles.

sodium hydroxide solution has to be heated to 850° C for 24 h to begin exhibiting reasonably well-defined *t*-ZrO₂ Bragg peaks. Whether this is a consequence of a hindered kinetics or the result of a greater thermodynamic stability due to the extremely small coherent domain size of the hydrous zirconia remains to be further explored.

The XRD patterns exhibited in Fig. 6 were used to evaluate the temperature dependence of the volume-weighted coherent domain size (crystallite size) of hydrous zirconia and the *t*-ZrO₂ and *m*-ZrO₂ obtained from it.²⁶ The calculations were performed using the peaks around $2\theta = 30.2^{\circ}$ for hydrous zirconia and *t*-ZrO₂ and $2\theta = 28.2^{\circ}$ for *m*-ZrO₂. The results are shown in Fig. 7.

For the sample as prepared, the coherent domain size is extremely small (1.5 nm) and is very similar to the particle size as determined from the analysis of TEM images of individual hydrous zirconia nanoparticles. It is noteworthy that the volumeweighted average crystallite size remains <3.5 nm even after a



Fig. 6. Room temperature X-ray powder diffraction patterns of hydrous zirconia previously submitted to successive 24 h thermal treatments at increasing temperatures. The tick marks below the patterns taken with the samples previously heated to 900° and 1300°C indicate the expected positions of the Bragg peaks for t-ZrO₂ and m-ZrO₂, respectively.

prolonged thermal treatment at 600°C. This is a key observation for future work aiming to obtain ceramic bodies made of nanocrystalline zirconia, as will be further discussed below.

Some experiments were also conducted with amorphous zirconium tungstate to determine the influence of particular features of the α -ZrW₂O₈ structure on the production of hydrous zirconia by soaking with sodium hydroxide solution. α -ZrW₂O₈ exhibits an open framework structure consisting of a tridimensional arrangement of corner-shared ZrO₆ and WO₄ polyhedra. For each WO₄ unit, three oxygen atoms are shared



Fig. 7. Volume-weighted average domain size versus temperature of thermal treatment of hydrous zirconia, t-ZrO₂ and m-ZrO₂. Dotted line is just a guide to the eye.





Fig. 8. SEM images of hydrous zirconia agglomerates at (a) low and (b) high magnification, and (c) optical microscopy image showing transparent, nearly fully densified polycrystalline agglomerates of nanocrystalline hydrous zirconia.

with Zr, while the fourth atom is bonded only to W and is referred to as terminal oxygen. Zirconium tungstate undergoes pressure-induced amorphization and previous results from O1s X-ray photoelectron spectroscopy give strong evidence that the amount of terminal oxygen atoms is greatly reduced in the amorphous phase.^{24,33} Accordingly, to verify to what extent the presence of terminal oxygen in α -ZrW₂O₈ may be determinant for the obtainment of hydrous zirconia by soaking zirconium tungstate with sodium hydroxide solution, the same experiment was performed with a sample of amorphous zirconium tungstate prepared at 7.7 GPa. Tungsten was lixiviated from amorphous ZrW₂O₈ the same way as with α -ZrW₂O₈, leading to the conclusion that the presence of terminal oxygen atoms in α -ZrW₂O₈ is not determinant for the successful production of hydrous zirconia.

Hydrous zirconia produced from zirconium tungstate exhibits a tendency to form micrometer-sized agglomerates of nanocrystalline particles. This can be seen in images obtained by SEM and optical microscopy, as shown in Fig. 8. The images shown in Fig. 8 exhibit what seem to be fully densified, nearly pore-free agglomerates, some of them even transparent to visible light. These images were taken from the white precipitate obtained after soaking zirconium tungstate with hot NaOH solution, dried overnight in a oven at 120° C, i.e., without any further heating that could promote sintering. Indeed, given the extremely small crystallite size of the hydrous zirconia reported in this work, the reduction of surface energy should be a very effective driven force for sintering, even at temperatures only slightly above room temperature. This observation, along with the fact that hydrous zirconia dehydrates under very mild conditions (for instance, by heating to 60° C under a vacuum of 10^{-5} mbar), suggests the possibility that fully densified, transparent ceramic bodies made of very small crystallite size anhydrous zirconia may be obtained under controlled conditions. With this aim in mind, further studies are being conducting trying to stabilize the hydrous zirconia nanoparticles in suspension.

IV. Conclusions

Hydrous zirconia nanoparticles were produced by soaking zirconium tungstate in boiling 1M NaOH solution for 5 h. The crystalline nature of the hydrous zirconia nanoparticles was investigated by TEM and XRD. Individual nanoparticles exhibited a narrow size distribution centered at 1.8 nm, in accordance with the volume-weighted coherent domain size of 1.5 nm, as determined by XRD. The extremely small crystalline domain size is probably responsible for the unusually high temperatures needed to promote the conversion from hydrous zirconia, $ZrO_2 \cdot 2H_2O_1$, into t-ZrO₂ (850°C) and m-ZrO₂ (1000°C) and, also, for the formation of nearly pore-free, micrometer-sized agglomerates. Further studies are needed in order to control the aggregation of the hydrous zirconia nanoparticles. Once a successful strategy has been devised, nanocrystalline hydrous zirconia suspensions could be used, among others possible applications, to prepare polymer-ceramic nanocomposites with high refraction index. Incorporation of phase stabilizers (such as yttrium) depends on finding a suitable precursor. Furthermore, controlled deposition from nanocrystalline hydrous zirconia suspensions by ultracentrifuging, followed by removal of hydratation water under very mild conditions could allow obtaining cold sintered bodies of anhydrous zirconia without coarsening, with mean crystallite size in the range of a few nanometers.

Acknowledgments

We thank Jim Walker, from Wah Chang Co. (Albany, OR), for the sample of zirconium tungstate. TEM analysis was performed in the Centro de Microscopia Eletrônica (CME) at the Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil. Thanks are due to Cássio R. de Almeida for his assistance and to Márcia R. Gallas (Laboratório de Altas Pressões e Materiais Avançados, Universidade Federal do Rio Grande do Sul) for the sample of amorphous zirconium tungstate.

References

¹C. Huang, Z. Tang, and Z. Zhang, "Differences between Zirconium Hydroxide (Zr(OH)₄ · *n*H₂O) and Hydrous Zirconia (ZrO₂ · *n*H₂O)," *J. Am. Ceram. Soc.*, **84** [7] 1637–8 (2001).

²J. Joo, T. Yu, Y. W. Kim, H. M. Park, F. Wu, J. Z. Zhang, and T. Hyeon, "Multigram Scale Synthesis and Characterization of Monodisperse Tetragonal Zirconia Nanocrystals," *J. Am. Chem. Soc.*, **125** [21] 6553–7 (2003).

³P. Li, I. W. Chen, and J. E. Penner-Hahn, "X-Ray-Absorption Studies of Zirconia Polymorphs. 1. Characteristic Local Structures," *Phys. Rev. B*, **48** [14] 10063–73 (1993).

⁴R. H. J. Hannink, P. M. Kelly, and B. C. Muddle, "Transformation Toughening in Zirconia-Containing Ceramics," *J. Am. Ceram. Soc.*, **83** [3] 461–87 (2000).

⁵R. Stevens., *Zirconia and Zirconia Ceramics;*, 2nd edition, Magnesium Elektron Ltd., Manchester, U.K., 1986.

⁶S. Jaenicke, G. K. Chuah, V. Raju, and Y. T. Nie, "Structural and Morphological Control in the Preparation of High Surface Area Zirconia," *Catal. Surv. Asiac.*, **12**, 153–69 (2008).

⁷S. Sômiya, F. Aldinger, N. Claussen, R. M. Spriggs, K. Uchino, K. Koumoto, and M. Kaneno, *Handbook of Advanced Ceramics*, Vol. 1, pp. 471–513. Elsevier Academic Press, London, U.K., 2003.

⁸J. Haines, J. M. Léger, S. Hull, J. P. Petitet, A. S. Pereira, C. A. Perottoni, and J. A. H. da Jornada, "Characterization of the Catunnite-Type Phases of Zirconia and Hafnia by Neutron Diffraction and Raman Spectroscopy," *J. Am. Ceram. Soc.*, **80** [7] 1910–4 (1997).

9S. Wang, Y. Zhai, X. Li, Y. Li, and K. Wang, "Coprecipitation Synthesis of MgO-Doped ZrO₂ Nano Powder," J. Am. Ceram. Soc., 89 [11] 3577-81 (2006).

¹⁶M. Trunec and K. J. Maca, "Compaction and Pressureless Sintering of Zir-conia Nanoparticles," J. Am. Ceram. Soc., **90** [9] 2735–40 (2007).

¹¹M. Rezaei, S. M. Alavi, S. Sahebdelfar, and Z. F. Yan, "Mesoporous Nanocrystalline Zirconia Powders: A Promising Support for Nickel Catalyst in CH4 Reforming with CO2," Mater. Lett., 61, 2628-31 (2007).

¹²M. Inoue, K. Sato, T. Nakamura, and T. Inui, "Glycothermal Synthesis of Zirconia-Rare Earth Oxide Solid Solutions," Catal. Lett., 65, 79-83 (2000).

¹³T. Yamaguchi, "Application of ZrO₂ as a Catalyst and a Catalyst Support," Catal. Today, **20** [2] 199–217 (1994). ¹⁴K. Tanabe, "Surface and Catalytic Properties of ZrO₂," *Mater. Chem. Phys.*,

13 [3–4] 347–64 (1985). 15 K. Tanabe and T. Yamaguchi, "Acid-Base Bifunctional Catalysis by ZrO₂ and

its Mixed Oxides," Catal. Today, 20 [2] 185-97 (1994).

¹⁶K. G. Kanade, J. O. Baeg, S. K. Apte, T. L. Prakash, and B. B. Kale, "Synthesis and Characterization of Nanocrystallined Zirconia by Hydrothermal Method," Mater. Res. Bull., 43, 723-9 (2008).

¹⁷V. F. Petrunin, V. V. Popov, Z. Hongzhi, and S. A. Korovin, "Stability of High-Temperature Phases of Ultrafine Zirconia," Glass Phys. Chem., 31 [4] 459-64 (2005).

¹⁸M. W. Pitcher, S. V. Ushakov, A. Navrotsky, B. F. Woodfield, G. Li, J. Boerio-Goates, and B. M. Tissue, "Energy Crossovers in Nanocrystalline Zirconia," *J. Am. Ceram. Soc.*, **88** [1] 160–7 (2005). ¹⁹E. Torres-Garcia, A. Peláiz-Barranco, C. Vásquez-Ramos, and G. A. Fuentes,

"Thermal and Structural Characterization of the $ZrO_{2-x}(OH)_{2x}$ to ZrO_2 Transi-

tion," J. Mater. Res., 16 [8] 2209–12 (2001).
²⁰H. Wang, G. Li, Y. Xue, and L. Li, "Hydrates Surface Structure and its Impacts on the Stabilization of *t*-ZrO₂," J. Solid State Chem., 180, 2790–7 (2007).
²¹M. K. Naskar and D. J. Ganguli, "Range of Metastability of Tetragonal Zir-in Compared Theorem Provide Theorem 2018 (2018).

1971-3 (1998).

²²D. A. Zyuzin, E. M. Moroz, A. S. Ivanova, and A. N. Shmakov, "Structure Characteristics of Disordered Zirconium Hydroxoxides," Cryst. Rep., 48 [3] 413-5 (2003).

²³C. A. Perottoni, "Transições de fase em compostos de estrutura aberta sob altas pressões"; Ph.D. Thesis, Instituto de Física-UFRGS, Porto Alegre, Brazil, 2000.

²⁴C. A. Perottoni and J. A. H. da Jornada, "Pressure-Induced Amorphization and Negative Thermal Expansion in ZrW2O8," Science, 280 [5365] 886-9

(1998). ²⁵T. Roisnel and J. Rodriguez-Carvajal, "WinPLOTR: A Windows Tool for Powder Diffraction Pattern Analysis," Mater. Sci. Forum, 378-381, 118-23 (2001).

²⁶R. Delhez, T. H. de Keijser, J. I. Langford, D. Louër, J. Mittemeijer, and E. J. Sonneved, "The Rietveld Method"; pp. 146–52 in *IUCr Monographs on* Crystallography, Edited by R. A. Young. Oxford University Press, Oxford, U.K.,

 ²⁷J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, A. D. Romig Jr., C. E.
²⁷J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, A. D. Romig Jr., C. E. Lyman, C. Fiori, and E. Lifshin, Scanning Electron Microscopy and X-Ray Microanalysis, 2nd edition, pp. 404-20. Plenum Press, New York, 1992.

²⁸J. L. Lábár, "Consistent Indexing of a (Set of) Single Crystal SAED Pattern(s)

with the ProcessDiffraction Program," *Ultranicroscopy*, **103**, 237–49 (2005). ²⁹S. Desgreniers and K. Lagarec, "XRDA—A Program for Energy-Dispersive X-Ray-Diffraction Analysis on a PC," *J. Appl. Crystallogr.*, **27**, 432–4 (1994).

S. Svehla, Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis, 5th edition, Longman Group Limited, New York, 1979, 510pp.

¹C. Huang, Z. Tang, Z. Zhang, and J. Gong, "Study on a New, Environmentally Benign Method and its Feasibility of Preparing Nanometer Zirconia Pow-

der," Mater. Res. Bull., **35** [9] 1503–8 (2000). ³²G. Davidson, Spectroscopic Properties of Inorganic and Organometallic Compounds, Vol. 35. RSC, Manchester, U.K., 2002, 243pp.

³³C. A. Figueirêdo, J. Catafesta, J. E. Zorzi, L. Salvador, I. J. R. Baumvol, M. R. Gallas, J. A. H. da Jornada, and C. A. Perottoni, "Compression Mechanism and Pressure-Induced Amorphization of y-ZrW2O8," Phys. Rev. B, 76 [18] 184201-7 (2007).