

A nearly pure monoclinic nanocrystalline zirconia

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Received 8 January 2005; received in revised form 28 February 2005; accepted 6 March 2005

Abstract

Generally, monoclinic zirconia is considered to be much more difficult to prepare at low temperatures and particularly in a pure state. The present work is the first example that shows that the hydrous zirconia formed by precipitation can yield a nearly pure nanocrystalline monoclinic zirconia at a temperature as low as 320 °C. The crystallite size of the monoclinic zirconia produced in the present work is around 15 nm, and it does not change appreciably as calcination temperature is increased from 320 to or above 400 °C. Such a small monoclinic crystallite arises from some of the chemical and physical factors built into the solution-gelation-xerogel process such as acidic preparation-pH, rapid precipitation, and moderate aging time and drying temperature, which result in a structure different from those of the existing zirconium hydroxides. In addition, the hydrous zirconia exhibits a unique thermal behavior in two respects: first, a sudden weight drop in the region of exothermic peak of the thermogravimetric curve is seen, suggesting that the main decomposition of the hydrous zirconia occurs in this region; second, there is an endothermic peak at high temperature in the differential thermal analysis curve, indicating the presence of coordinated water in the hydrous zirconia.

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Keywords: Nanocrystalline zirconia; Crystallization; Thermal behavior; Monoclinic structure

1. Introduction

An intense interest in zirconia-based ceramics results from a number of key characteristics. These include excellent refractoriness and chemical resistance, good mechanical strength, high fracture toughness and hardness, large ionic conductivity, low thermal conductivity at high temperature together with relatively high coefficient of thermal expansion, and a promising combination of significant dielectric constant and good thermal stability and resistance to thermal shock. These useful properties make them have great potential for structural and functional applications such as advanced structural transformation-toughened ceramics for wear parts, engine and machine components, cutting and

abrasive tools; piezoelectric and dielectric ceramics; sensors/probes for oxygen transport and detection; solid electrolytes for solid oxide fuel cells and high-temperature water-vapor electrolysis cells; catalysts for automotive exhaust cleaning and the partial oxidation of hydrocarbons; pigments; mixed-conductors exhibiting both oxygen ion and electronic conductivity for oxygen separation membranes and electrocatalyst; thermal barrier coatings; optical coatings; a buffer layer between superconducting film and silicon substrate; a gate-dielectric material in modern integrated-circuit technology; and a good host for nuclear wastes.

Zirconia exists in three crystalline forms of monoclinic, tetragonal and cubic structures at atmospheric pressure. The martensitic transformation from the tetragonal to the monoclinic structure has great importance in ceramic and catalytic applications since it is the basis for transformation toughening and has a significant effect on catalyst activity. Although monoclinic

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zirconia is the thermodynamically stable phase for pure zirconia at temperatures up to 1170 °C, generally, upon increasing calcination temperature, most amorphous zirconia precursors convert to the tetragonal phase first and then transform to the monoclinic phase at a higher temperature (~600 °C); that is, the metastable tetragonal phase forms in preference to monoclinic phase during crystallization of amorphous hydrous zirconia into nanocrystalline zirconia. Thus, the thermodynamically stable monoclinic variety seems to be much more difficult to prepare at low temperatures and particularly in a pure state, as indicated in the literature [1–3]. During the last decades an active research has been undertaken in different laboratories worldwide in order to induce or delay the phase transformation of tetragonal crystallites toward the monoclinic ones. As a result of the intense work done, however, only an exception to this generalization was found; that is, nanocrystalline monoclinic zirconia could be produced from acidic zirconium salt solution (pH < 2) by hydrothermal treatments including an extensive refluxing [4–10]. The hydrothermal technique requires pressure (20–100 MPa), temperature (150–650 °C), long run duration (1–14 days), and additives such as NaOH, KF, HNO₃, and H₂SO₄. Here we show an easy route to a nearly pure nanocrystalline monoclinic zirconia. Furthermore, it is quite interesting to point out that the precursor of the monoclinic zirconia, i.e., a hydrous zirconia, which is formed under acidic conditions, has a structure different from the three types of the existing zirconium hydroxides, which were precipitated under near-neutral and alkaline conditions, and hence can exhibit a thermal behavior much different from that previously known.

2. Experimental

2.1. Methods

Analytical reagent-grade ammonia was used as received from Shanghai Chemical Reagent Plant. Analytical reagent-grade zirconium oxychloride octahydrate was bought from the Shanghai Chemical Reagent Plant and further purified by recrystallization before use.

The zirconium oxychloride octahydrate was dissolved in deionized water so that the final concentration of zirconium was 38.76 g l⁻¹ (0.42 M). Fifteen milliliter of the zirconyl chloride solution was added to 300 ml deionized water in a glass or Teflon beaker, and then concentrated aqueous ammonia was added rapidly to the solution with constant stirring until pH 4.5. The resultant precipitate was aged in the mother liquor for 1 day. After filtration it was washed several times with dilute ammonia and hot deionized water (80 °C)

until chloride ions were no longer detectable in the washing water (AgNO₃ test), and then dried at 90 °C for 30 h. The dried precipitate also called xerogel looked brownish.

2.2. Analyses and measurements

The zirconium and other metals in the xerogel were assayed by both inductively coupled plasma-atomic emission spectroscopy using an IRIS Advantage/1000 ICP-AES spectrophotometer (Thermo Jarrel Ash Corporation, USA) and energy dispersive spectrometry using a FALCON model EDX-ray spectrophotometer (EDAX Company, USA). The determination of hydrogen, nitrogen, and oxygen in the xerogel was made by a Perkin–Elmer Series II CHNS/O Analyzer 2400, USA. Chlorine in the xerogel was determined by energy dispersive spectrometry using a FALCON model energy dispersive X-ray spectrophotometer (EDAX company, USA).

X-ray diffraction (XRD) data were collected by using a Bruker-AXS D8 Advance diffractometer (Germany) equipped with a scintillation counter and a graphite monochromator. The xerogel was heated to several temperatures in air, with each temperature being held for 3 h. As the sample was cooled to room temperature, the XRD pattern was recorded by scanning it over a 2θ range of 20–90° at a scan speed of 0.2 s/step with an increment of 0.02°/step, and utilizing CuK α radiation at 40 kV and 40 mA. The crystallization was determined as the point at which Bragg peaks first appeared. The identification and quantification of monoclinic (M), tetragonal (T) and cubic (C) zirconia were accomplished by comparison of the XRD data to the Powder Diffraction File (file numbers 79-1771 and 78-0047 for tetragonal and monoclinic phases, respectively) using the Bruker Eva.exe program. To determine the mean crystallite size of the tetragonal and monoclinic phases, we selected the two strongest peaks assigned to the monoclinic phase (28.2°, indexed as 1 $\bar{1}$ 1, and 31.5°, indexed as 111) and the reflection corresponding to the tetragonal phase (30.3°, indexed as 101). Their half-height widths were determined through a least-squares best fit with Lorentzian profiles and baseline correction when needed.

The xerogel was examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a thermal analyzer (Universal V2.4F TA Instruments, USA). These experiments were conducted up to 800 °C with a heating rate of 10 °C min⁻¹ in air.

A nitrogen sorptometer (micromeritics ASAP 2010, USA) was used to measure the specific surface area and micropores volume of the xerogel and its pyrolysis products from the adsorption isotherms determined for N₂ at liquid nitrogen temperature using the BET and

Dubin equations. Specific surface area was measured following degassing at 200 °C for 0.5 h.

3. Results and discussion

3.1. Crystallization

3.1.1. General

Formation of hydrous zirconia by forced hydrolysis under acidic conditions, aqueous precipitation under alkaline conditions, and hydrolysis/condensation of alkoxide has been studied extensively experimentally and theoretically [11–25]. However, much less is known about the precipitation of hydrous zirconia under acidic conditions [26–31] than that under alkaline conditions, because potential difficulties lie in washing the precipitate formed at low pH values to remove anions and consequently discriminating the role of precipitation chemistry from the formation of zirconia crystal phases [15]. However, neither nitrogen nor chlorine ions were detected in the hydrous zirconia prepared by the present process.

Generally, the tetragonal phase of zirconia forms preferentially to the monoclinic phase during crystallization of amorphous hydrous zirconia. At low calcination temperatures (<400 °C), only the tetragonal phase is present. As the calcination temperature increases to or above 400 °C, both monoclinic and tetragonal phases are detected, the latter being predominant. Finally, above approximately 800 °C, complete transformation occurs, and only monoclinic zirconia is observed. A significant exception to this generalization occurs in the present work, as follows.

3.1.2. Unusual

The X-ray diffraction pattern (Fig. 1a) of the xerogel shows only very broad peaks, indicating an absence of long-range order, whereas the XRD pattern (Fig. 1b) of the xerogel heated to 310 °C exhibits that diffraction peaks begin to emerge, and reveals a just-crystallized mixture of predominantly monoclinic zirconia (70%) with some tetragonal zirconia (30%). This is the first example that shows that the hydrous zirconia formed by precipitation yields a predominantly monoclinic structure coexisting with the tetragonal one as soon as crystallization starts at a low temperature (310 °C). At such a low temperature, the hydrous zirconia can be decomposed and crystallized into a predominantly monoclinic zirconia, suggesting the weaker bond energy of the hydroxyls present in the hydrous zirconia precipitated under acidic conditions and hence the hydroxyls, which can play a crucial role in stabilizing the tetragonal structure at room temperature, should more easily be removed from the hydrous zirconia formed under acidic conditions than from it precipitated under near-neutral or alkaline conditions, resulting in the early appearance of the monoclinic structure. At the crystallization temperature (310 °C), the monoclinic crystallite size is about 17 nm and the tetragonal one, 28 nm. The monoclinic crystallite is much smaller than the tetragonal one with which it co-exists. This result is not consistent with the traditional view that a critical particle size effect is responsible for the stability of the tetragonal and monoclinic structures. If the critical particle size limit of 30 nm is exceeded, the tetragonal particles are transformed into the monoclinic ones [32]. Above the critical particle size of 18 nm the monoclinic structure is stable [33]. The crystallite size of the monoclinic particles was smaller than the tetragonal

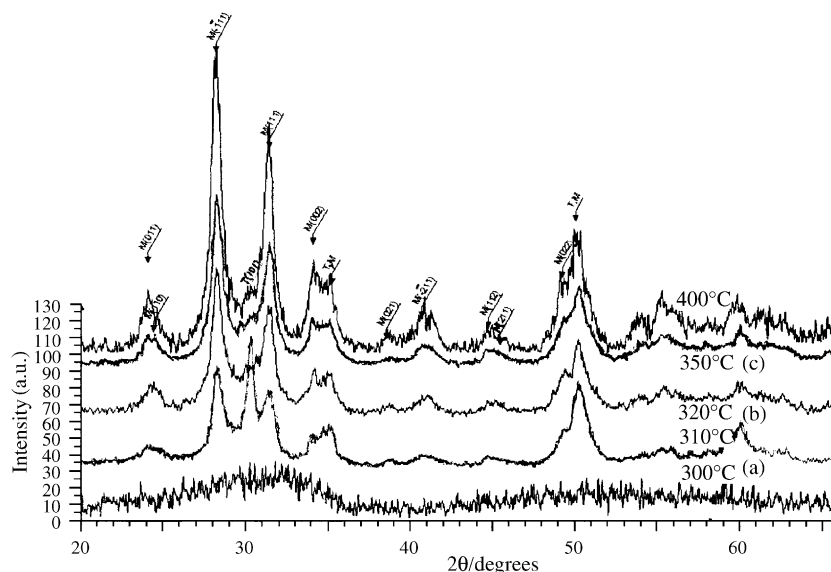


Fig. 1. XRD patterns of the hydrous zirconia calcined at 300, 310, 320, 350 and 400 °C.

particles that underwent transformation. This ‘strange’ result was also reported by other investigators in preparing nanoparticulate zirconia with other methods and explained tentatively in terms of twinning and/or lattice strain of the monoclinic crystallite [34]. In the present work, the existence of the small monoclinic crystallite is attributed to a lowering of the surface free energy of the zirconia nanoparticles derived from the hydrous zirconia precipitated under acidic conditions, causing the destabilization of the metastable tetragonal structure toward the monoclinic one at such a low temperature [6,7,9,35,36]. The state of the particle surface may be a significant factor in the stabilization of the tetragonal and /or monoclinic structures. The hydrous zirconia formed in the present work exhibits a $167\text{ m}^2\text{ g}^{-1}$ of specific surface area (BET), $0.08\text{ cm}^3\text{ g}^{-1}$ of total pore volume (at $P/P_0 = 0.98$), and $0.03\text{ cm}^3\text{ g}^{-1}$ of micropore volume. A nearly pure monoclinic nanocrystalline zirconia with a $74\text{ m}^2\text{ g}^{-1}$ of surface area can be produced from the hydrous zirconia at low temperature, $350\text{ }^\circ\text{C}$. In addition, in the present work the removal of foreign anions from the precipitate was effected by washing with dilute ammonia and hot deionized water ($80\text{ }^\circ\text{C}$). The resultant anionic vacancies can play an important role in the tetragonal-to-monoclinic phase transformation. The adsorption of oxygen triggers this phase transformation, and the adsorption of water leads to the decrease in the difference between the surface free energies of tetragonal and monoclinic zirconia, resulting in the small monoclinic crystallite. First-principles studies on the surfaces of zirconia indicated that the most likely surface structure is $[\text{OH}^-, \text{H}^+]$ with terminal and bridging hydroxyl groups and the last removal of the adsorbed water occurs at about $457\text{ }^\circ\text{C}$ [37], and that the stoichiometric tetragonal (111) and monoclinic ($\bar{1}11$) are the most stable surfaces and the surface energy is considerably anisotropic, thus depressing the tetragonal–monoclinic phase transition temperature in small particles [38], or in other words, supporting our results.

When the temperature ($310\text{ }^\circ\text{C}$) is slightly raised to $320\text{ }^\circ\text{C}$, the XRD pattern (Fig. 1c) shows an essentially pure monoclinic zirconia. The diffraction peaks show broadening as to be expected for nanocrystallites. The crystallite size calculated by XRD measurement is around 15 nm , and it does not change appreciably as calcination temperature is increased from 320 to or above $400\text{ }^\circ\text{C}$. In the present work the chemical and physical factors such as pH, addition rate of ammonia, and aging time and drying temperature built into the solution-gelation-xerogel process have a significant influence upon the low-temperature formation of nanocrystalline monoclinic zirconia. A detailed discussion follows.

In the present work the addition of aqueous ammonia to a highly acidic zirconyl salt solution results in the formation of amorphous hydrous zirconia precipitate

owing to the reduced solubility of zirconia with increase in pH. It is, therefore, understandable that the formation and phase distribution of the zirconia polymorphs must have been related to the effect of solubility and in turn to solution pH. Furthermore, the preparation of the hydrous zirconia based on neutralization evidently constitutes a chemical shock and thereby induces very rapid polymerization of zirconium species in solution, generating polymeric structures that ultimately precipitate as gels. It is known that the tetrameric species $[\text{Zr}_4(\text{OH})_8 \cdot 16\text{H}_2\text{O}]^{8+}$ is a major species in acidic solutions, but other polynuclear positively charged species, for example, monomeric or trimeric species also exist in acidic solutions. The initial nucleation of monoclinic zirconia is favored by the association of the soluble tetrameric species under acidic conditions, because formation of tetragonal phase nuclei would be less efficient the lower the pH [36]. In addition, the monomeric or trimeric species may be polymerized with the tetrameric species to form a random structure. The dissolution-reprecipitation process may yield the thermodynamically stable monoclinic structure due to the distortion introduced by monomeric or trimeric species in the polymer [9,39]. The gels exhibit high entropy, partial hydration, and entrapped counterions owing to the rapid polymerization of these species. It is necessary to take longer time or higher temperatures to do extensive reconstruction for crystallization of three-dimensional polymers. It was observed in the present work that the final pH of the solution coexisting with the precipitate, after the precipitation procedure was accomplished, would be changed with the aging of the precipitate formed under acidic conditions. The pH value could be reduced by a factor of ca. 0.5 after aging for 1 day, and essentially stabilized after aging for 2 days. This behavior indicates that the extensive structural rearrangement of the precipitate occurs on aging. The anions Cl^- originally present in the precipitate were displaced by hydroxyls. In addition, when the OH^- bond changes to the O^{2-} bond, H^+ ions are released to solution. The consequent reduction in pH of the mother liquor permits crystallinity to develop, because acidic solutions may facilitate crystal formation. Aging the precipitate formed under acidic conditions brings about the transformation of amorphous gel particles into a mixture containing tetragonal and predominantly monoclinic crystallites.

3.2. Thermal behavior

3.2.1. Precipitation under neutral and alkaline conditions

It is well known that there are three types (α , β and γ) of zirconium hydroxide: α , $[\text{Zr}_4(\text{OH})_{16}]$; β , $[\text{Zr}_4\text{O}_2(\text{OH})_{12}]$; and γ , $[\text{Zr}_4\text{O}_4(\text{OH})_8]$ or $[\text{ZrO}(\text{OH})_2]$ in the literature [3,11,22,23,40–42]. These zirconium hydroxides, which are also referred to as hydrous zirconia,

show a single exothermic peak at around 420 °C and no endothermic peak above 120 °C in DTA curve; in the region of the exothermic peak, hardly any weight loss is observed from TGA curve, and hence the exothermic peak is attributed to the transition from an amorphous to a tetragonal metastable phase of zirconia, i.e., a topotactic crystallization of tetragonal zirconia on nuclei present in the amorphous phase. It is, however, quite interesting to point out that the hydrous zirconia formed in the present work has a structure different from those of the existing zirconium hydroxides, and therefore can exhibit a thermal behavior much different from that previously known, as follows.

3.2.2. Precipitation under acidic conditions

The DTA curve of the hydrous zirconia investigated shows three-step decomposition behavior: two endothermic and one exothermic decomposition processes (Fig. 2). The first endothermic process occurring from room temperature to 138 °C, amounting to a loss of 10.5% of its initial weight, is attributed to a loss of physically adsorbed water. The second endothermic process is complete at about 244 °C, and amounts to a loss of 6.1% of its initial weight. Such a high-temperature dehydration indicates some water molecules present in the hydrous zirconia to be a coordinated water, and therefore this weight loss arises from the split out of the coordinated water. The precipitation-derived product, in particular the aged precipitate, is undoubtedly more hydrous. It is, furthermore, obvious that water molecules nested within the framework of the aged hydrous zirconia are more strongly bound than those present in the non-aged samples. The removal of water from the hydrous zirconia is the rate-limiting step in crystallization of amorphous zirconia. The structurally bound water plays an important role in the structure of the precipitate because not only the oxo group but also the coordinated water would compete with hydroxy groups to fit in with zirconium atoms,

resulting in the products with various compositions and structures. The relative amount of oxygen, hydroxyl, and water in hydrous zirconia depends on the rate of precipitation and on the source and chemistry of zirconium salts used. The present work has demonstrated that the acidic preparation-pH, rapid precipitation, and moderate aging time can have a substantial impact on the incorporation of water into the amorphous precipitate structure and on the temperature at which the amorphous state transforms to the crystalline one, as mentioned in the preceding section and in this section. In addition, water present during calcination can catalyze the tetragonal to monoclinic phase transformation of zirconia [34].

After dehydration, the hydrous zirconia is progressively decomposed into amorphous zirconia due to dehydroxylation with increasing temperature and a sharp exothermic peak appears around 450 °C. The exothermic event is accompanied by weight drop (about 1.4%), indicating that the main decomposition occurs in the region of the exothermic peak. Support for this contention can be seen from the DTG curve (Fig. 3). The DTG curve displays a remarkable peak around the exothermic temperature, 450 °C, showing the presence of an appreciable weight loss, and a plateau before the peak, indicating that hardly any weight loss occurs. The exothermic peak with weight change is assigned to a rapid release of bound hydroxyl groups at a higher temperature, by which amorphous zirconia is suddenly formed and crystallized into essentially pure monoclinic zirconia, as evidenced by the X-ray diffraction patterns (Fig. 1) and DTG curve (Fig. 3). The crystallization and glow phenomenon (exotherm) for the existing zirconium hydroxides occur at the same temperature. However, it may be found from Figs. 1 and 2 that the crystallization of the hydrous zirconia formed in the present work has begun before the exotherm starts. Crystallization may be considered as reorganization of small particles into an X-ray crystalline form, wherein no significant heat is

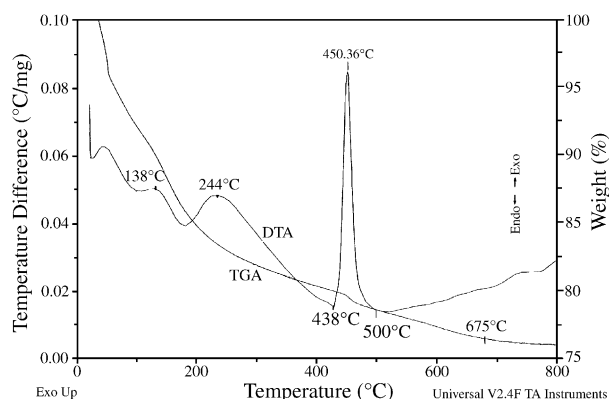


Fig. 2. DTA and TGA curves of the hydrous zirconia.

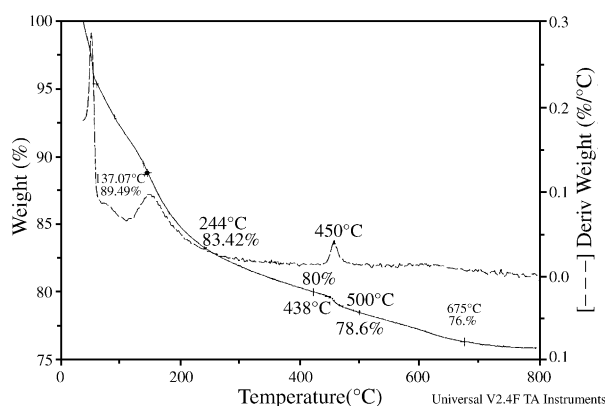


Fig. 3. DTA and TGA curves of the hydrous zirconia.

released and hardly any weight loss is observed, whereas the glow phenomenon is due to the exotherm, wherein a sudden weight drop takes place, indicating a fast formation and crystallization of amorphous zirconia by rapid release of bound hydroxyl groups. Finally, the TGA curve reveals that the weight loss is complete at 675 °C, which is equal to 24% of the initial weight of the xerogel sample. In other words, the zirconia content in the hydrous zirconia investigated is 76%, i.e., zirconium 56.3%, which is close to the value found from the elemental analysis.

3.3. Structure

The elemental analysis gave the following results (wt%): Zr 55.5, H 2.5, and no nitrogen and chlorine ions were present in the xerogel. Upon subtracting the weight corresponding to physically adsorbed water, the xerogel can be represented by an empirical formula: $Zr_2O_3(OH)_2 \cdot H_2O$. The zirconium atom does not give up electrons; instead, electrons may either be bound to its ligands covalently or accepted by the zirconium, producing a negative charge, which repels hydroxyl groups. This condition leads to preferential formation of oxo and aquo groups rather than true hydroxides [43]. It is, therefore, reasonable to form the zirconium oxyhydroxide $Zr_2O_3(OH)_2 \cdot H_2O$ in the present work. It can be thought of as the product of dimerization of γ -type zirconium hydroxide $[ZrO(OH)_2]$ with the formation of coordinated water. Fig. 4 shows a possible structural model, namely the hydrous zirconia is described as an

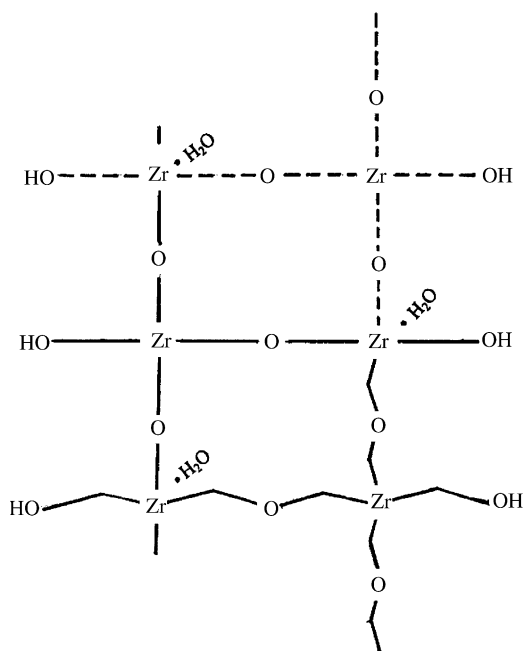


Fig. 4. Two-dimensional representation of polymerization of the hydrous zirconia via oxolation. (Solid, dashed, and bent lines represent three units of $Zr_2O_3(OH)_2 \cdot H_2O$, respectively.)

open polymer in which individual units and a pair of zirconium atoms in each unit are linked by oxo bridges. The structure is characterized by less hydroxyls, only one oxo bridge between zirconium atoms, and presence of coordinated water, indicating that the hydrous zirconia is a precursor of monoclinic zirconia. It is obvious that the hydrous zirconia formed in the present work has a structure different from those of the existing zirconium hydroxides. Such contrast in the structure is clearly associated with the preparation methods used. Many researchers [2,12,15,16,23,44], who studied the hydrous zirconia precipitated under alkaline conditions, indicated that hydrous zirconia is an unstable substance whose composition depends strongly on the conditions of preparation. In the present work, special attention has been paid to some of the chemical and physical factors built into the solution-gelation-xerogel process such as acidic preparation-pH, rapid precipitation, and moderate aging time and drying temperature in order that an essentially pure nanocrystalline monoclinic zirconia can be prepared by precipitation at low temperature. Preparation-pH has a marked influence on the crystal phase formation of the initially calcined zirconia and also on crystallite growth and subsequent tetragonal-monoclinic transformation. Precipitation under acidic conditions can behave much differently from that under alkaline conditions, giving rise to the unusual crystallization and thermal behavior of the hydrous zirconia investigated, as discussed in the preceding sections and in this section. When precipitation is brought about rapidly, the precipitate is not able to grow in a more orderly fashion so that the formation of the monoclinic structure is favored on heating rather than the tetragonal one. In addition, precipitation rate can have a substantial impact on the amount of water incorporated into the amorphous precipitate structure, and the coordinated water, in turn, plays an important role in the structural transformations and thermal behavior of the amorphous hydrous zirconia during calcination, as indicated above. Aging brings about the coordinated water and oxolation in the structure of the hydrous zirconia, promotes crystal growth, and transforms the amorphous gel particles into a crystalline product exhibiting a predominantly monoclinic structure, as discussed in the preceding sections and in this section. Finally, a drying temperature of 90 °C was chosen because the thermodynamic analysis of the ZrO_2-H_2O system has shown that zirconium hydroxide is a stable solid phase below about 85 °C; above 85 °C, monoclinic zirconia becomes thermodynamically stable [8]. The loss of water from the double hydroxo bridges to form oxo bridges occurs above 80 °C and this reaction generates embryonic oxide nuclei [14,45]. Therefore, the predominantly monoclinic structure of the hydrous zirconia has emerged at an earlier stage namely during the drying process before crystallization starts. This

result is supported by the Raman spectrum (not shown) of the hydrous zirconia in the present work. In summary, these preparation conditions emphasized by the present work have a significant influence on the structure of the resulting hydrous zirconia, favor the formation of the monoclinic phase rather than the tetragonal one, and therefore give rise to the unusual crystallization and thermal behavior. In addition, the importance of the starting zirconium salt should not be overlooked in the preparation of hydrous zirconia [1,12]. Also, it is possible that the source and chemistry of zirconium salts used is related to the formation and phase distribution of the zirconia polymorphs after calcination of hydrous zirconia because the solution chemistry of zirconium is complex and not well understood.

4. Conclusions

A nearly pure nanocrystalline monoclinic zirconia has been prepared by precipitating a hydrous zirconia from zirconium oxychloride solution with ammonia at pH 4.5 at room temperature, aging the precipitate in mother liquor for 1 day, and then filtrating and washing it with dilute ammonia and hot deionized water (80 °C), drying at 90 °C, and calcining at 320 °C. This is the first example that shows that the hydrous zirconia formed by precipitation can yield a nearly pure nanocrystalline monoclinic zirconia at a temperature as low as 320 °C. This temperature is about 280 °C lower than that usually required to obtain a pure monoclinic zirconia by precipitation. In addition, in comparison with hydrothermal treatments they require pressure (20–100 MPa), temperature (150–650 °C), long run duration (1–14 days), and additives such as NaOH, KF, HNO₃, and H₂SO₄. It is, therefore, evident that the present process offers a cost-effective route to a pure nanocrystalline monoclinic zirconia with distinct advantages in terms of simplicity, time- and energy-saving, and minimal environmental impact.

The hydrous zirconia at the very onset of crystallization (310 °C) yields a predominantly monoclinic structure (70%) coexisting with the tetragonal one (30%). The monoclinic crystallite size is about 17 nm and the tetragonal one 28 nm. Upon heating the hydrous zirconia to 320 °C, a pure nanocrystalline monoclinic zirconia is produced with a crystallite size of 15 nm, and it does not change appreciably as calcination temperature is increased from 320 to or above 400 °C. It is, therefore, clear that our data do not support the traditional view that a critical particle size effect is responsible for the stability of the tetragonal and monoclinic structures. In the present work special attentions have been paid to some of the chemical and physical factors built into the solution-gelation-xerogel

process such as acidic preparation-pH, rapid precipitation, and moderate aging time and drying temperature. These preparation conditions have a significant influence on the structure of the resulting hydrous zirconia, favor the formation of the monoclinic phase rather than the tetragonal one, and give rise to the unusual crystallization and thermal behavior.

A more descriptive formula for the hydrous zirconia would be Zr₂O₃(OH)₂·H₂O. A possible structural model is proposed, by which the hydrous zirconia is described as an open polymer in which individual units and a pair of zirconium atoms in each unit are linked by oxo bridges. The structure is characterized by less hydroxyls, only oxo bridge between zirconium atoms, and presence of coordinated water, indicating that the hydrous zirconia is a precursor of monoclinic zirconia.

The DTA and TGA curves of the hydrous zirconia are seen to be unique in two respects: first, a sudden weight drop in the region of the exothermic peak is seen, suggesting that the main decomposition of the hydrous zirconia into amorphous zirconia occurs in this region; second, there is an endothermic peak at high temperature, indicating the presence of coordinated water in the hydrous zirconia. In addition, in accordance with the XRD patterns and the TGA curve, the crystallization and exotherm of the hydrous zirconia do not occur at the same temperature. The crystallization has begun before exotherm starts, suggesting that the crystallization of the hydrous zirconia takes place on a wide range of temperatures.

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