



# Control of the nanocrystalline zirconia structure through a colloidal sol-gel process



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## ABSTRACT

A simple method to synthesize tetragonal zirconia stabilized at ambient temperature is developed and allows the monitoring of the tetragonal-monoclinic transition *via* a colloidal sol-gel process. By increasing the pH of an aqueous solution consisted of a zirconium precursor and a complexing agent (acetylacetonate), a colloidal sol and then a gel can be formed under slightly acidic condition. After a drying step, tetragonal zirconia is easily obtained with an adequate thermal treatment at low temperature. The tetragonal-monoclinic transition occurs when the calcination temperature is increased. The relationship between the crystallite size, the crystallographic structure and the thermal treatment has been investigated by X-Ray Diffraction and the behaviour of the system from the gel state to the final powder has been studied by using Small Angle X-Ray Scattering and thermal analysis techniques. We demonstrate that compared to a chemical precipitation route, this colloidal sol-gel process allows the nanostructure of the material to be controlled due to the formation of primary nanoparticles. The presence of these nanoparticles makes possible the specific determination of the zirconia crystallographic phase through an accurate control of the nanostructure during the thermal treatment.

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## 1. Introduction

Thermodynamically, pure bulk zirconia has three stable crystal phases depending on the temperature: a monoclinic phase ( $m\text{-ZrO}_2$ ,  $P2_1/c$  space group) below 1172 °C, a tetragonal phase ( $t\text{-ZrO}_2$ ,  $P4_2/nmc$  space group) from 1172 to 2347 °C and a cubic phase ( $c\text{-ZrO}_2$ ,  $Fm3m$  space group) above the latter value. Generally, the crystal phase strongly influences the zirconia properties [1]. This is especially true for  $t\text{-ZrO}_2$ , which has both acidic-basic surface properties [2] and different redox states and which is widely used as a catalyst and catalyst support in several reactions, including alcohol dehydration, acetylation of alcohols and amines, CO/CO<sub>2</sub> hydrogenation, and alkane isomerization as well as for the selective oxidation of alcohols and alkanes [3]. The  $t\text{-ZrO}_2$  displays a high performance in the design of super-acidic catalysts, which is not the case for the monoclinic phase [4]. That is why the synthesis of  $t\text{-ZrO}_2$

is the subject of different works since several years. However, a large number of these procedures, such as plasma spraying [5] and combustion [6], hydrothermal [7] or microwave assisted sol-gel [8] processes, prove to be relatively tedious or even quite expensive. Furthermore, the use of extreme conditions (high-temperature and/or high-pressure) can also be problematic as well as the use of toxic zirconium alkoxides.

The development of easier ways is thus currently under investigation and some synthesis routes were recently reported based on sol-gel or precipitation reactions [9]. These routes rely particularly on two techniques. The stabilization of  $t\text{-ZrO}_2$  at low temperature is traditionally achieved in bulk materials by adding a dopant, such as Y<sup>3+</sup> and Mg<sup>2+</sup> [10], or by decreasing the crystallite size to obtain a nanocrystalline structure [11]. Indeed, the crystallite size reduction of zirconia to the nanometre scale (typically under 10 nm) is known to stabilize the tetragonal phase [11]. The smaller the particle size, the higher the surface tension, which results in an increased internal pressure in the particles responsible for the stabilization of the tetragonal phase [12]. The synthesis of undoped  $t\text{-ZrO}_2$  with a nano-crystallite size is generally achieved from zirconium alkoxides [13]. Inorganic zirconium salts (*i.e.*, zirconyl chloride) have also

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been explored to prepare t-ZrO<sub>2</sub> [14], but require a long synthesis procedure of 10 days. The formation of the tetragonal phase is predominantly dependent on the nature of the precursor salt, the synthesis method, and the crystallite size of zirconia.

In this work, we report the synthesis of a t-ZrO<sub>2</sub> phase at low temperature as well as a thermal-controlled monitoring of the tetragonal-monoclinic transition. A colloidal sol-gel method using a zirconyl nitrate salt precursor and acetylacetone as the complexing agent [15,16] is used to avoid precipitation and allow the nanoparticles and the gel formation. The nanostructure and crystalline state of the zirconia particles from the colloidal gel are investigated by Small-Angle X-ray Scattering (SAXS), High-Resolution Transmission Electron Microscopy (HRTEM), Thermal Analyses and X-ray Diffraction (XRD). The relationship between the phase structure and the crystallite size is highlighted. The roles of the zirconium precursor concentration and the amount of acetylacetone as well acting towards the stabilization of the nanoparticles are studied. These two effects have been linked to the required thermal treatment in order to obtain t-ZrO<sub>2</sub> or m-ZrO<sub>2</sub>. A comparison between the sol-gel route and the pure precipitation route, from the same precursor solution and with the same thermal treatment, is discussed. This study presents a synthesis route to obtain a t-ZrO<sub>2</sub> phase in the absence of a dopant by carefully controlling crystallite growth through an innovative acetylacetone-based colloidal sol-gel method.

## 2. Experimental procedure

### 2.1. Synthesis of ZrO<sub>2</sub> powders

The different operations and reactions were performed at room temperature and under an ambient atmosphere. ZrO(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich) was used as the zirconium precursor and deionized water as the solvent. Three zirconium concentrations have been studied (0.1, 0.16 and 0.22 M). Acetylacetone (acacH) (Sigma-Aldrich) was used as a complexing agent and added to the solutions after dissolution of the zirconium precursor. We defined *K*, a molar ratio as  $K = [\text{acacH}]/[\text{Zr}]$ . The pH of these initial solutions were determined and are given below. We noted that higher zirconium concentrations resulted in lower pH solutions. Furthermore, the addition of acetylacetone slightly increased the pH value. Table 1.

Next, the pH of each solution was adjusted by the addition of ammonia (3 M) under vigorous stirring. The system behaviour (gelation or precipitation) does not strongly depend on the zirconium concentration, but does depend strongly on the *K* value.

For *K* = 0.5 or 1, a white precipitate is formed that re-dissolves after a few minutes when the pH is increased. A colloidal suspension of amorphous oxyhydroxide is obtained up to pH = 4. The pH values were specifically chosen in order to keep the same synthesis conditions (*i.e.* lightly acidic conditions) and simultaneously to observe the gelation in a maximum time of few hours. These colloidal suspensions may form gels after a certain period of time depending on the system parameters used (*i.e.*, precursor concentration, acacH concentration, and pH) [17].

For *K* = 0, no complexing agent is added, and when the pH is increased, we observe the spontaneous formation of a white

precipitate at any zirconium concentration. The pH was increased to 5.5 to allow complete precipitation. This precipitate was then recovered by filtration. We noticed that less ammonia was necessary to trigger the precipitation (compared to the system with acacH) due to the high reactivity of the zirconium solution.

Finally, both powders or gels were dried at 80 °C overnight in ambient air and treated at different temperatures between 300 and 1200 °C for 2 h (heating rate of 10 °C/min).

### 2.2. Characterizations

#### 2.2.1. pH measurements

The pH was determined using a glass combination electrode connected to a pH-meter (SevenMulti, Mettler Toledo) and calibrated at pH 2, 4, 7 and 9.

#### 2.2.2. X-ray diffraction (XRD)

The crystallographic phase of the zirconia powders was determined at room temperature by X-ray Diffraction (XRD). Experiments were performed on a diffractometer (D8 Advanced, Bruker) in a Bragg-Brentano geometry with a Ni-filtered Cu-K $\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ) operated at 40 kV and 40 mA. The  $2\theta$  angles were scanned from 10 to 80° at a rate of 0.2°/min. The crystalline size ( $D_c$ ) of the powders was estimated by the Debye-Scherrer formula, as given in the following equation [18]:

$$D_c = \frac{k\lambda}{\beta \cos \theta}$$

where  $\beta$  is the breadth of the observed diffraction line at its half-intensity maximum; *k* is the so-called shape factor, which usually takes a value of 0.9; and  $\lambda$  is the wavelength of the X-ray source used in XRD. The crystallite size determination was based on the (111) and (-111) reflections for the m-ZrO<sub>2</sub> and on the (111) for the t-ZrO<sub>2</sub>.

The volume fractions of the monoclinic ( $V_m$ ) and tetragonal ( $V_t$ ) phases were estimated by integration of the intensities of the (111) and (-111) peaks of m-ZrO<sub>2</sub> ( $I_m$ ) and the (111) peak of t-ZrO<sub>2</sub> ( $I_t$ ) [19] and using a ratio *x* defined as:

$$x = \frac{I_m(-111) + I_m(111)}{I_m(-111) + I_m(111) + I_t(111)}$$

$$V_m = \frac{1.311x}{1 + 0.311x}, \quad V_t = 1 - V_m$$

#### 2.2.3. High-Resolution Transmission Electron Microscopy (HRTEM)

High-Resolution Transmission Electron Microscopy (HRTEM) images were taken on a microscope (1200EXII, Jeol) operated at 120 kV. The samples were first prepared by dispersing the powder in absolute ethanol and then transferring them onto carbon-coated copper grids.

#### 2.2.4. Small angle X-ray scattering (SAXS)

Small Angle X-ray Scattering (SAXS) experiments were

**Table 1**  
Summary pH values before and after the addition of ammonia and associated gelation time as a function of the initial zirconium concentration and the molar ratio *K*.

[Zr]	0.1 M			0.16 M			0.22 M		
<i>K</i>	0	0.5	1	0	0.5	1	0	0.5	1
Initial pH	1.33	1.36	1.39	1.18	1.22	1.27	1.04	1.11	1.12
Final pH	5.5	6	6	5.5	5.5	6	5.5	5	6
Gelation time	/	150 min	Few hours	/	100 min	Few hours	/	20 min	Few hours

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