Thermal and structural characterization of the $ZrO_{2-x}(OH)_{2x}$ to ZrO_2 transition

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The exothermic process that occurs around 700 K during calcination of $ZrO_{2-x}(OH)_{2x}$, associated with the crystallization of the low-temperature tetragonal metastable phase of ZrO_2, was analyzed using x-ray diffraction, high-resolution thermogravimetric analysis (TGA), nitrogen adsorption, and modulated differential scanning calorimetry (MDSC). High-resolution TGA allowed us to determine the water loss, resulting from condensation of OH^- groups. The amount was 0.137 wt% in our case, equivalent to 1.7×10^{-2} mol of H_2O/mol of ZrO_2. That corresponds to about one –OH group per nm^2 being lost in that process. By using MDSC we determined that the change in enthalpy ($\Delta H_{global} = -15.49$ kJ/mol of ZrO_2) was the result of two parallel contributions. One of them was reversible and endothermic ($\Delta H_{rev} = 0.11$ kJ/mol of ZrO_2), whereas the other was irreversible and exothermic ($\Delta H_{irrev} = -15.60$ kJ/mol of ZrO_2). The variability and magnitude of the exotherm, as well as the fact that the accompanying weight loss is so small, are consistent with a mechanism involving the formation of tetragonal nuclei, rather than global crystallization, and hence depend on the number of nuclei so formed.

I. INTRODUCTION

Zirconia-based materials possess special characteristics for practical applications. They have high thermal stability, low thermal conductivity, and high resistance to corrosion. As a result, they are used as refractory materials, pigments, piezoelectric devices, ceramic capacitors, oxygen sensors, and as catalysts, among other uses. In the latter case, low-temperature phases are commonly used, in order to retain a satisfactory surface area.

Three crystalline phases of pure zirconia are usually considered in the literature:[1,2] the monoclinic, stable up to about 1440 K; the tetragonal phase, which appears during annealing treatment above 1440 K; and the cubic phase, which is stable between 2640 to 2950 K.[2–4] However, by controlling the processing, it is possible to synthesize a porous or dense polycrystalline zirconia with a metastable tetragonal structure.[5,6]

Processing usually involves precipitation from a Zr salt solution, followed by calcination in the 673 to 1173 K range. The formation and stability of the tetragonal phase have been the object of numerous discussions and the mechanism does not seem to be yet elucidated. What is known is that the initial precipitate, a hydrous material, denominated here $ZrO_{2-x}(OH)_{2x}$, usually undergoes an exothermic transition around 673 K. Among the different explanations that have been proposed, the most plausible ones invoke the similarity between the structure of the amorphous phase and that of the tetragonal crystals,[7] a topotactic crystallization of tetragonal zirconia on nuclei present in the amorphous phase,[8] or the presence of stabilizing strains[9] which lower the surface free energy of the tetragonal phase below that of the monoclinic phase for crystallite sizes less than a critical

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value.[5,10] In spite of these proposals, to our knowledge there is not yet a fully accepted interpretation of the structural and thermal phenomenology of the so-called crystallization process or glow exotherm. In this work we present quantitative results that give a better understanding of that phenomenon.

II. MATERIALS AND METHODS

A. Preparation

The $ZrO_{2-x}(OH)_{2x}$ system was prepared by hydrolysis of a $ZrOCl_2$ ($ZrOCl_2 \cdot 8H_2O$, Aldrich, Milwaukee, USA, >98 wt%, containing <0.5 wt% Hf) solution (0.5 M) via controlled addition of NH_4OH (28%, J.T. Baker, Xalostoc, Mexico) under constant agitation until pH = 10. The addition was carried out in 1 h. The obtained precipitate, a white gelatinous solid, was filtered and washed several times by dispersion in a NH_4OH solution (pH = 10) to eliminate Cl^- ions. We tested the wash waters with a solution of $AgNO_3$ (3 M) until we had less than 10 ppm of residual Cl^- ions. The resulting white gel was then dried at 383 K for 15 h, leading to our starting $ZrO_{2-x}(OH)_{2x}$ material. We prepared samples with differing degrees of conversion to ZrO_2 and different ZrO_2 phase ratios by heating $ZrO_{2-x}(OH)_{2x}$ at a 5 K/min rate until the target temperature was reached. That temperature was then held constant for 1 h before removing the sample from the oven.

B. Characterization

1. X-ray diffraction

The powder samples were analyzed at room temperature by x-ray diffraction (XRD) (Siemens diffractometer, Germany, D500 Model) with Cu K_α radiation at a scanning rate of 0.003° s^{-1} and a Ni filter. The generator conditions were 30 kV and 20 mA in the angular range 5–70° 2θ.

To determine the mean crystallite size of the tetragonal and monoclinic phases, we selected the two largest bands assigned to the monoclinic phase (28.4°, indexed as 11–1, and 31.6°, indexed as 111) and the reflection corresponding to the tetragonal phase (30.3°, indexed as 111). We determined their half-height widths through a least squares best fit with Lorentzian profiles and baseline correction, when needed. Instrumental broadening was corrected using quartz as the reference. The mean size of the crystallites was then calculated using the Scherrer equation.

2. Thermal analysis

The thermogravimetric analysis (TGA) was carried out using a high-resolution thermobalance (TGA High-Resolution, TA Instruments, Wilmington, DE, TG-2950 Model). The temperature range studied was 296 to 1073 K, at a rate of 50 K/min with an instrumental resolution of 5 and a N_2 flow rate of 100 ml/min. The sensitivity of the balance was 10^{-7} g.

The data of modulated differential scanning calorimetry (MDSC) (TA Instruments MDSC-2920) were obtained under the following conditions: initial temperature of 253 K, modulation of ± 0.318 K each 60 s, with isotherms for 5 min and ramps of 2 K/min until 773 K in a N_2 atmosphere. In this technique a heat flow differential scanning calorimetry (DSC) cell arrangement is used, but a sinusoidal modulation (heating/cooling) is overlaid on the standard linear temperature ramp. As a result, there are three heating-related parameters that can be used to improve on DSC: heating rate, amplitude of modulation, and modulation frequency. MDSC determines the total heat flow and its reversible and nonreversible components, and provides increased understanding of complex transitions in materials.

3. Brunauer–Emmett–Teller surface area

The Brunauer–Emmett–Teller analysis (BET) surface area was determined by physical adsorption of N_2 at 75.5 K (boiling point of N_2 in Mexico City) using automated equipment (Micromeritics, Atlanta, GA, Model ASAP-2000). The samples were evacuated previously at 473 K and 1.4×10^{-4} Pa for 24 h.

III. RESULTS AND DISCUSSION

A. Structural analysis

X-ray traces of $ZrO_{2-x}(OH)_{2x}$ calcined below 573 K show only wide bands in the 18 to 40° 2θ and 40 to 70° 2θ ranges (Fig. 1). As the calcination temperature increases to or above 673 K, both monoclinic and metastable

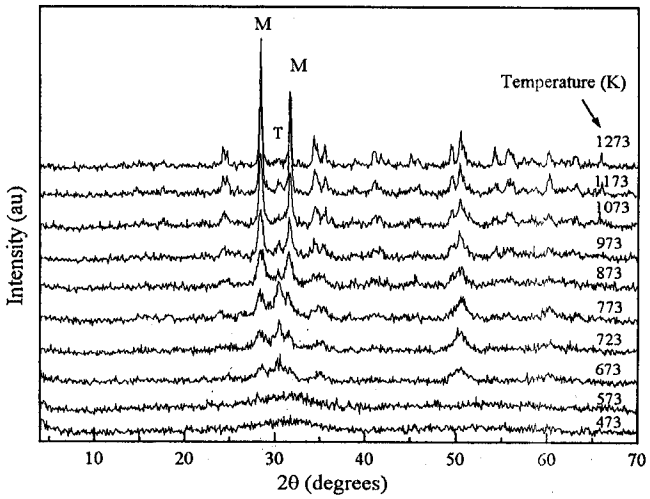

FIG. 1. XRD patterns accompanying the structural transformation of $ZrO_{2-x}(OH)_{2x}$ to ZrO_2 as a function of the calcination temperature. (M and T indicate peaks characteristic of monoclinic and tetragonal ZrO_2, respectively.)

tetragonal phases are detected, the latter being predominant. Further increases in the calcination temperature lead to an essentially complete transformation to the monoclinic structure, which is reported as the stable phase in the temperature range studied here, i.e., below 1440 K.[2,11]

From our analysis of specific XRD lines, we found that the mean crystallite size of the metastable tetragonal phase was in the 4 to 5 nm range, and it did not change appreciably up to 1273 K, suggesting the existence of a critical size. At the same time, the mean crystallite size of the monoclinic phase increased from roughly 3 to 35 nm, as shown in Fig. 2. The critical size of the metastable low-temperature tetragonal crystallites of ZrO_2 prepared in this study is below that of other reports, where a value of 10 nm was mentioned.[5] This appears to be caused by differences in the synthetic methods used. Growth of the monoclinic crystallites is in agreement with previous studies.[6]

The crystallite growth process was accompanied by a decrement in surface area.[5,11,12] $ZrO_{2-x}(OH)_{2x}$ dried at 473 K exhibited a BET surface area of 310 m^2/g, approximately. The surface area decreased significantly as the calcination temperature rose, being about 4 to 6 m^2/g at 1073 K. This corresponds to the densification of the structure accompanying the loss of micro- and mesopores.

Our results are consistent with a growth mechanism involving an upper critical size for the tetragonal phase. Tetragonal crystallites can grow until they reach that limit and any further growth is accompanied by a transition to the monoclinic structure. Monoclinic particles are not limited in size during further sintering and growth.[6] The group of Alivisatos has reported a similar observation in the case of unsupported CdS crystallites.[13]

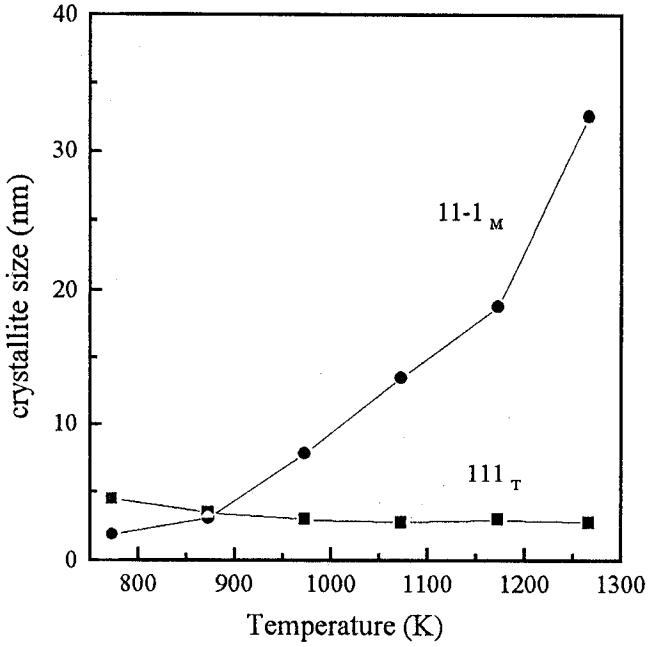

FIG. 2. Effect of the calcination temperature on the average crystallite size. Circles indicate size calculated using the 11–1 reflection of the monoclinic phase, and squares indicate size calculated using the 111 reflection of the metastable tetragonal phase.

B. Glow exotherm

It is known that around 700 K an exothermic process occurs during calcination for $ZrO_{2-x}(OH)_{2x}$.[6,14] That temperature and process are commonly referred to as a crystallization temperature and as a glow exotherm. The energy evolved is not a constant, being a function of the preparation method.[15] It ranges between −15 and −34 kJ/mol of ZrO_2.[6] Our results of MDSC, shown in Fig. 3, are within that range. We determined $\Delta H_{global} = -15.49$ kJ/mol of ZrO_2, and the maximum in the exotherm occurred at 670 K in our case. MDSC indicated that the overall exotherm was the combination of an endothermic reversible process ($\Delta H_{rev} = 0.11$ kJ/mol of ZrO_2), and an exothermic irreversible component ($\Delta H_{irrev} = -15.60$ kJ/mol de ZrO_2). This simply means that the exotherm is primarily the result of an irreversible process, without having further structural information at this stage. To understand the process we performed a high-resolution TGA.

We observed that the shape of weight versus temperature curve is associated with the continuous dehydration of the solid. The total weight loss at 800 K relative to the initial weight was of about 25% in our sample, and it was a function of the preparation conditions during precipitation, as they affect the O/OH ratio in the starting oxyhydroxide.[15] The resulting formula for our starting material was $ZrO_{0.86}(OH)_{2.28}$, given $x = 1.14$.

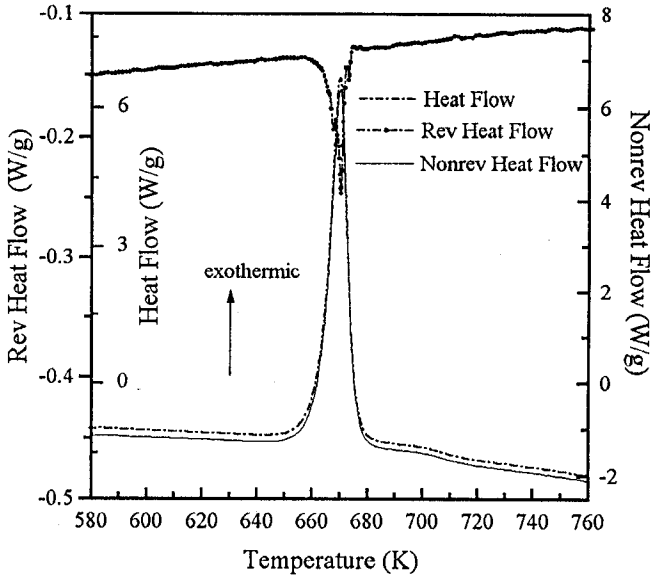

FIG. 3. MDSC analysis of $ZrO_{2-x}(OH)_{2x}$ previously dried at 383 K for 15 h.

Although the glow exotherm for ZrO_2 has been reported to be a transition without weight loss,[6,11] by using high-resolution TGA we determined the existence of a small weight loss at 720 K (Fig. 4). It corresponds to the glow exotherm under the conditions of the TGA experiment. The weight loss appears to correspond to the formation of H_2O by condensation of surface –OH groups. We estimated that about one –OH group was lost per 100 Zr atoms. On a surface area basis, roughly one –OH per nm^2 was lost at that point. This certainly is not a massive modification of the structure of the crystallites.

The combined results involving XRD, high-resolution TGA, MDSC, and surface area measurement indicate that the exothermal process in our $ZrO_{2-x}(OH)_{2x}$ material probably corresponds to a nucleation step of the tetragonal crystallites, i.e., a topotactic crystallization of tetragonal zirconia on nuclei present in the amorphous phase. This is consistent with the Raman spectroscopy study reported by Urlacher and Mugnier.[3] Once tetragonal nuclei are formed, they grow until reaching a limit about 5 nm. Any further growth of a particular tetragonal crystallite is accompanied by a transition to the thermodynamically more stable monoclinic phase. Growth of this crystallite is not restricted now, as observed in Fig. 2. As the temperature increases even further, the number of tetragonal crystallites decreases and the material gradually transforms to the monoclinic phase.

The variability in the magnitude of the glow exotherm can now be understood, as the total energy evolved depends upon the number of tetragonal nuclei formed. This explanation is also consistent with the effect of surface additives, such as WO_x groups,[15] upon the glow exotherm, as their presence retards the onset of the exotherm by nearly 100 K. The absence of further thermal effects as the tetragonal–monoclinic transformation occurs appears to be caused by sensitivity limitations, given the gradual nature of the process as the temperature increases. That is not a classical phase transition, but rather a kinetically controlled transformation.

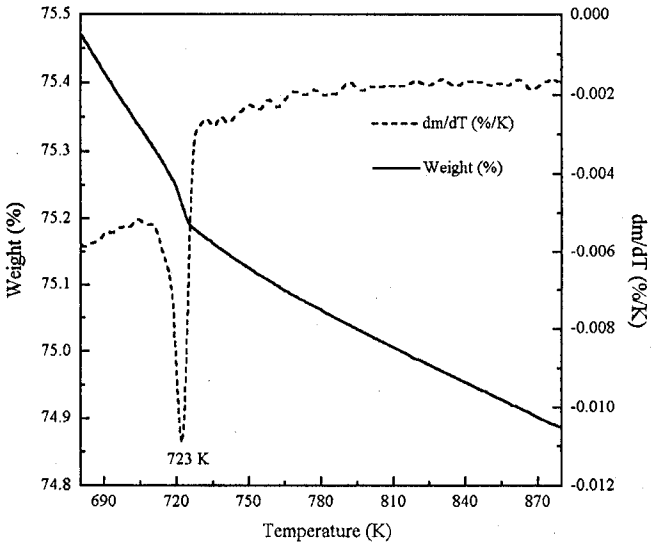

FIG. 4. High-resolution TGA of $ZrO_{2-x}(OH)_{2x}$ in N_2: thermogravimetric curve and its corresponding derivative.

IV. CONCLUSIONS

Use of high-resolution thermal analyses coupled with structural information indicates that the exothermic process occurring near 700 K during calcination of zirconium oxyhydroxide is consistent with a mechanism involving nucleation of tetragonal crystallites, rather than full crystallization of the sample. The magnitude of the exotherm depends then upon the number of nuclei formed, being –15.49 kJ/mol ZrO_2 in our case. By using XRD we determined a critical size of about 5 nm for the tetragonal crystallites. Further growth of those crystallites results in a kinetically controlled transition to the monoclinic phase, whose crystallites are not limited in size. This mechanism offers an acceptable explanation of the variations in the magnitude and temperature at which the glow exotherm occurs during the synthesis of pure or doped metastable tetragonal ZrO_2.

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