



Influence of starting precursors and synthesis methods on the physiochemical properties of zirconia



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ABSTRACT

Under identical and judiciously pre-optimized synthesis conditions, the influence of different combinations of zirconium sources and/or post treatment conditions on structural properties, thermal stability, phase composition and morphology of zirconia has been investigated. High surface area tetragonal zirconia could be synthesized in a cost-effective manner from 1 M solution of zirconium oxynitrate at pH 11 using aqueous ammonia solution as a precipitant when calcined at 400 °C for 3 h. Irrespective of the preparation method, pH and starting precursor, zirconia samples prepared without digestion contained dominant monoclinic phase with some traces of tetragonal phase when calcined at 700 °C. Even though there is linear decrease in surface area with increase in the crystallite size for each sample as a function of calcination temperature, no co-relation between the surface area and crystallite size could be achieved. SEM images show agglomerated and irregular shape particles between 10 to 20 μm.

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1. Introduction

Zirconia is a remarkable material, which has attracted a great deal of attention from scientists, technologists and researchers. The use of zirconia, from both scientific and industrial application point of view requires high surface area, crystalline tetragonal phase and suitable pore structure for catalysis applications. However thermal treatments and/or high temperature reactions results in loss of surface area and transition from the tetragonal to the monoclinic phase causing sintering and deactivation of the catalyst, thereby the stability of tetragonal phase is crucial. The concentration and transformation among tetragonal, monoclinic and cubic phases depend on synthesis procedure and thermal treatment conditions [1,2]. Numerous methods have been explored to obtain tetragonal zirconia with superior surface area and suitable pore structure [3–8]. Taguchi et al. showed that the selection of the precursor and tuning of the reaction temperature can control the crystalline phase and the particle size of the zirconia nanoparticles prepared by rapid hydrothermal method from zirconium ethoxide and zirconium hydroxide as the precursors using sub- or supercritical water at temperatures

between 200 and 500 °C for 10 min [9]. Nanocrystalline zirconia with tetragonal phase having pore-size of ~4 Å and a high surface area of 340 m² g⁻¹ was synthesized by Chakravarty et al. using zirconyl chloride and ammonium hydroxide in alkaline medium [10]. Recently, much attention was paid to the synthesis using a surfactant-assisted route to obtain high surface area with uniform pore size distribution [11,12]. A more recent article in which Sliem et al. prepared zirconia nanoparticles using nonhydrolytic (avoiding sol–gel) pyrolytic synthesis technique based on suited metal-organic precursors/surfactant combinations which may be useful in situ synthesis of colloidal catalysts [13]. Although, several synthesis routes have been developed and reported, no systematic comparison study was reported with regard to optimized synthesis parameters using different starting precursors on the pathway of structural development and properties such as textural/structural, thermal stability and morphology of pure zirconia materials. Also most of the above mentioned synthesis routes to prepare stable high surface area tetragonal zirconia are complicated and require tedious procedures and close control of reaction parameters. In this context, facile synthesis routes are highly desired, especially for the practical applications of zirconia. Having said that the two most commonly used synthesis procedures: Precipitation and sol–gel have been selected. The synthesis details and materials obtained from these two synthesis routes are compared and discussed in detail.

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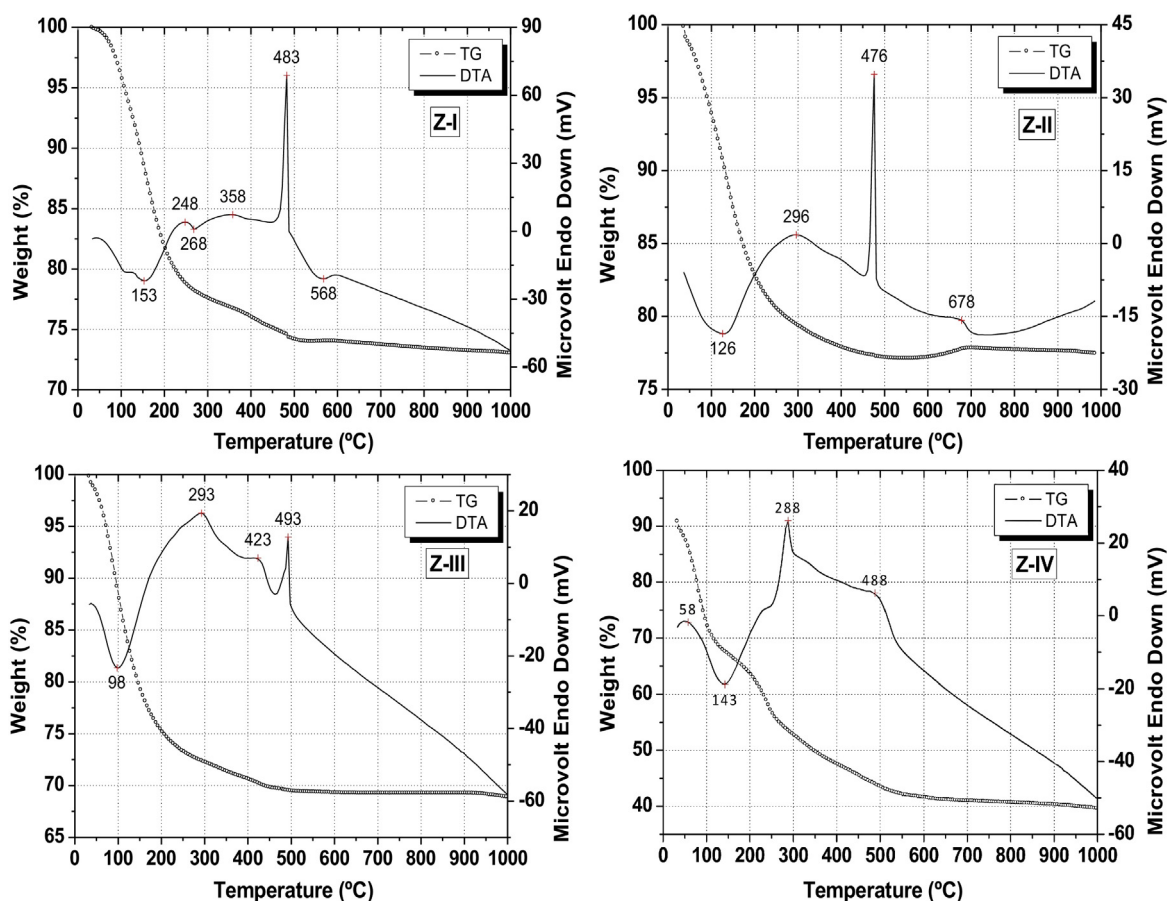


Fig. 1. TG-DTA of as-synthesized zirconia samples Z-I, Z-II, Z-III and Z-IV.

2. Experimental

2.1. Materials

The starting zirconium precursors used were zirconium oxy-nitrate [$\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, 98%, Loba Chemie, India] and zirconium (IV) butoxide [$\{\text{Zr}[\text{OC}(\text{CH}_3)_3\}_4\}$, 80% in *n*-butanol, Sigma-Aldrich, USA]. Pluronic 123 [ethylene oxide (EO_{20})-propylene (PO_{70})-ethylene oxide (EO_{20}), molecular weight –5800, Sigma-Aldrich, USA] and ammonium hydroxide [NH_4OH , 28% NH_3 in H_2O , Merck] were used as surfactant and precipitation agent, respectively.

2.2. Synthesis methods

Zirconia was prepared using two different synthesizing methods:

2.2.1. Preparation of zirconia by precipitation method

In a typical synthesis, ammonium hydroxide solution was added drop wise to an aqueous solution of zirconium oxy-nitrate

under rapid stirring. After precipitation, the slurry was aged overnight (~12 h) in the mother liquor with constant stirring. This precipitate was filtered and washed several times with de-ionized water. The final product was firstly dried overnight at room temperature then at 100 °C for 12 h. The hydroxide precipitate was divided into equal proportions and calcined in air at 400, 500, 600 and 700 °C for 3 h. These samples were designated as Z-I_4C, Z-I_5C, Z-I_6C and Z-I_7C, respectively. The letter Z denotes ZrO_2 . The numbers 5C, 6C, 7C and 8C are referred to the calcination temperatures (C – Calcination). The non-appearance of the denotation 4C, 5C, etc. indicates the samples are not calcined and are in as-synthesized form. In order to investigate the influence of different zirconium source materials on the quality of zirconia materials another batch (Z-II) was prepared by precipitation technique using zirconium *tert*-butoxide instead of zirconium oxy-nitrate under identical set of synthesis conditions. Another set (Z-III) of zirconia samples were prepared with digestion to evaluate the effect of digestion on the thermal and structural properties. Zirconium oxy-nitrate was used as starting precursor for the preparation of Z-III samples. Here in the wet un-

Table 1
Details of the zirconia samples prepared by different synthesis procedure and precursors.

Sr. no	Sample name	Synthesis method	Zirconium source	Surfactant	Synthesis pH	Digestion (h)
1	Z-I	Precipitation	Zirconium oxy-nitrate	Nil	11	Nil
2	Z-II	Precipitation	Zirconium butoxide	Nil	11	Nil
3	Z-III	Precipitation	Zirconium oxy-nitrate	Nil	11	12
4	Z-IV	Sol-gel	Zirconium butoxide + zirconium oxy-nitrate	P123	2	Nil

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