In-situ evaluation of particle size distribution of ZrO$_2$-nanoparticles obtained by sol–gel

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ARTICLE INFO

ABSTRACT

In this study the in-situ synthesis of zirconia via sol–gel was investigated in order to relate the influence of the processing parameters on particle size distribution. Zirconium n-propoxide was used as the precursor, n-propanol as solvent and several parameters were investigated, such as pH, reaction medium, synthesis time and temperature. The particle sizes and the polydispersion of colloidal dispersions were determined in situ using dynamic light scattering. In acetic medium, the particle size remained mostly below 100 nm. With the introduction of NaCl, the maximum particle size reached 71 nm. For other reaction media (HNO$_3$ and without acid or base), the largest particle size was in the order of micrometers. The comparison of the different synthesis routes investigated did not enable us to observe one trend related to increased particle size when compared to reaction times in the synthesis of zirconia. This work aims to show how the reaction medium influence in obtaining a colloidal dispersion with nanometric sizes obtained from the sol–gel process.

1. Introduction

It is well-known that colloidal dispersions have a high area/volume ratio regarding the electrical loads on their surfaces, when exposed to polar solvents. The electrical potential between the interface of the particle surface decreases more rapidly as the ionic strength increases, since the electric double layer is compressed towards the surface by the concentration of ions of the solution [1]. One possible explanation for the suspension's stability is the formation of particle clusters that occur because of hydrophilic and electrolytic forces [2].

Cluster formation can be modeled as two charged spheres approaching each other. If the kinetic energy exceeds the repulsive potential of the electric charge, the particles aggregate. There are two limiting regimes for the aggregation of colloidal particles. The first one is related to diffusion-limited colloid aggregation (DLCA), where a stable aggregate is formed every time two particles collide. The aggregation rate in this case is fully determined by the number of collisions per time. In the second regime, the repulsive barrier due to surface charges or steric effects hinders the aggregation and a large number of collisions are required in order to form a stable coagulate. This is the so-called reaction-limited colloid aggregation (RLCA) [3].

Typically, ZrO$_2$-nanoparticles are used as model substance in the study of agglomeration processes in colloidal suspensions [4]. The

sol–gel method and co-precipitation from solutions form, together with hydrolysis and colloidal processes, the chemical method category [5]. The chemical methods, and especially the sol–gel method, are characterized by flexibility, the usage of non-aggressive solutions, low cost, and relative simple reaction conditions. The sol–gel method is based on molecular synthesis of nanoparticles where during the process of nanopowder formation close control over the nucleation and growth of the particles is required because the particles easily adhere and form agglomerates [5].

The methods that have been reported in the literature for synthesizing zirconia particles (include the following: forced hydrolysis of zirconium in organic salt solutions, precipitation from solutions of inorganic salt or alkoxide complexes, and hydrothermal method [6]), have been widely employed. In order to control the formation of sub-micrometer particles, including YSZ powders, chemical methods, such as sol–gel processing, have been applied and investigated extensively.

Sol–gel processing involves hydrolysis and polycondensation of a precursor and the subsequent formation of a gel [7]. Heat treatment of the formed gel results in a crystalline network structure and, depending on the gelling solution, may be formed as fibers, monoliths, thin and thick film coatings, and powders. The ability to control the parameters of the final product, such as purity and microstructure, and to consolidate the particles at relatively low temperatures, are some of the advantages of the sol–gel method in relation to materials produced via conventional synthesis routes [8]. The literature [9–11] suggests that gelation of hydrated zirconium oxide takes place in two steps: step

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one — formation of sol-primary particles, their growth, hydrolysis, and polymerization; and step two — coagulation of sol and formation of polymeric gel.

Liu et al. [12] report on the marked similarity between the self-assembly of metal nanoparticles and reaction-controlled step-growth polymerization. The nanoparticles act as multifunctional monomer units, which form reversible, noncovalent bonds at specific bond angles and organize themselves into a colloidal polymer. They report an approach for the quantitative prediction of the structural characteristics of linear, branched, and cyclic ensembles of nanoparticles, in addition to their structural isomers. They hypothesized that nanoparticles act as multifunctional monomer units that, in a process analogous to step-growth polymerization, organize themselves into macromolecule-like assemblies. The growth of nanoparticle chains was described by the kinetics and statistics of step-growth polymerization, which, for a particular time, allowed the prediction of the aggregation number and the size distribution of nanoparticle ensembles, similar to the degree of polymerization and polydispersity index (PDI) of polymers, respectively.

The main aim of this work is to determine the influence of the reaction conditions in situ, to obtain zirconia by the sol–gel method. Different acids during hydrolysis (pH), temperature and reaction time were studied in relation to particle size distribution.

2. Material and methods

2.1. Synthesis of the zirconia gels

The samples were obtained by hydrolysis of 1.21×10^{-2} mol n-propoxyde of zirconium (Du Pont) in 1.03 mol n-propanol (Merck) in the presence of acetic acid (8.75×10^{-2} mol) (Merck), 5.82×10^{-4} mol of nitric acid (Merck), or in a neutral medium (no acid and/or base), under magnetic stirring and a temperature of 27 °C and/or at 70 °C under reflux, in the case of compositions with acetic acid. The influence of sodium chloride in an acetic acid medium was investigated by replacing the deionized water (0.71 mol) by a solution of NaCl

0.071 mol $\cdot$ L^{-1}, previously standardized (Method of Mohr) [13]. The samples for light scattering analysis were taken at different times. The flow chart of Fig. 1 shows the methodology used.

2.2. Characterization of the dispersions by light scattering and zeta potential

Particle size (PS), polydispersity and zeta potential measurements were performed by dynamic light scattering (DLS), at 20 °C, in a Zetasizer Nano ZS, ZEN 3500 model (173° and 532 nm) and the data express the results of the extent of the entire sample, covering all the populations in the sample (detection range is 0.6 nm to 6 μm size measurement particle). For the evaluation of the zeta potential, the equipment was adjusted to operate in the detection range of 5 nm to 10 μm. Since more than one population was observed, the samples were considered to be polydispersed. The content of every population was also determined by data analysis. The samples for light scattering measurements were prepared by dilution of 20 μL of the particle suspensions in 1 mL n-propanol, used as received (Merck). For the evaluation of the zeta potential, the equipment was adjusted to operate in the detection range of 5 nm to 10 μm. For the determination of zeta potential, 20 μL of sample was diluted into 1 mL of aqueous NaCl 10^{-3} mol$\cdot$L^{-1}.

3. Results and discussion

It is well known that the effect of temperature on the size of the particles can be linked to changes in the polarization (slight changes) that lead to aggregation. This is a consequence of the physicochemical properties of the particle surface. By increasing the temperature, the zeta potential may vary, affecting the stability of particles in solution [14]. Consequently, the population of larger particles may increase. The particle size distribution as a function of sample and temperature is shown in Fig. 2. Fig. 2(A) shows the predominance of a population with a particle size < 100 nm, in longer times (for longer periods of agitation — 60 and 120 min), the majority of the population provides
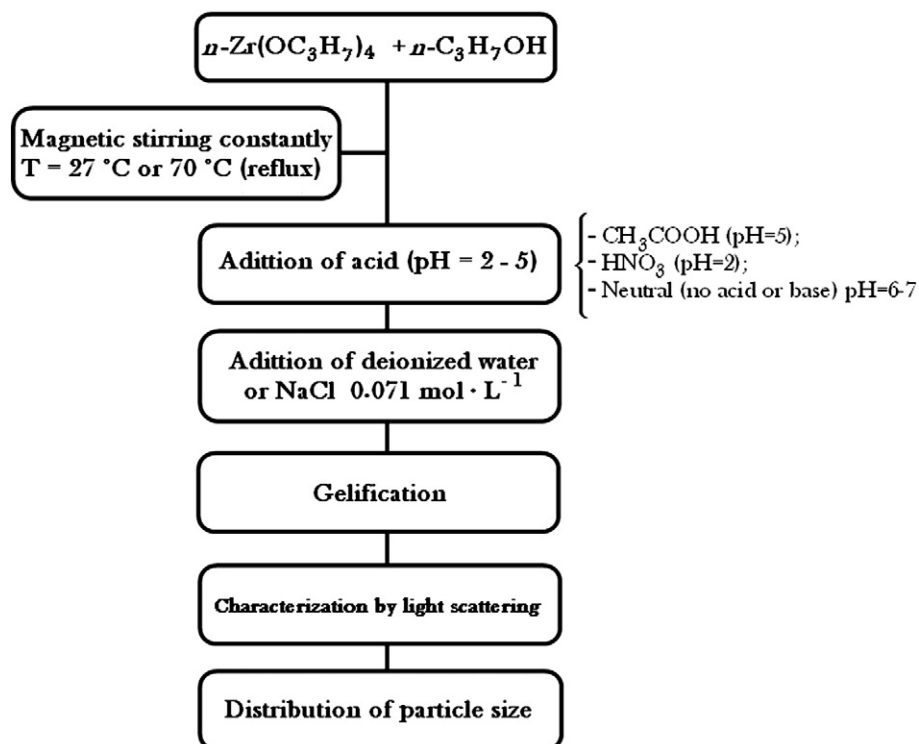

Fig. 1. Flow chart of the synthesis and characterization of interfacial dispersion of zirconia.