

**EFFECT OF SYNTHESIS CONDITIONS AND pH ON
STABILIZATION OF METASTABLE TETRAGONAL ZIRCONIA**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE
in
PHYSICS

By

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Rourkela – 769 008

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Under the Guidance of

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CERTIFICATE

This is to certify that the thesis entitled, “**Effect of synthesis conditions and pH on stabilization of metastable tetragonal zirconia**” submitted by Miss **Prajna Priyadarshinee Rout** in partial fulfillments for the requirements for the award of **Master of Science** Degree in **Physics** at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance at the Department of Ceramic Engineering.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

Date:8th May 2009

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ABSTRACT

The present work deals with the effect of different synthesis conditions, pH and concentration of sodium borohydride (NaBH_4) on the stabilization of tetragonal Zirconia nanopowders through reduction technique. Nanocrystalline t- ZrO_2 has technologically significant material that finds extensive use as catalyst, oxygen sensor and structural components. In this work ZrO_2 nanoparticles are synthesized using reduction technique at two different concentration of reducing agent. These techniques also promote the stabilization of t-phase of ZrO_2 at nano level at moderate temperature which is one of the primary objectives of this work. For reduction technique, the Zr-salt is reduced by addition of strong reducing agent (NaBH_4). This reduction process includes three different synthesis processes occurring at different pH. Here the main objective is to stabilize the t- ZrO_2 through gelation (low pH), precipitation (High pH) and reduction at constant pH by using NaBH_4 . From XRD results, stabilization of metastable t- ZrO_2 was observed up to 600°C for both gelation and precipitation but in case of reduction at constant pH it is purely amorphous at both the concentrations of NaBH_4 (0.5M, 5M). However with increase in temperature both tetragonal and monoclinic phases are observed in case of both gelation and precipitation whereas in case of reduction at constant pH pure t- ZrO_2 is observed at 800°C . So it has been concluded that at low concentration with increase in pH the crystallite size decreases but at high concentration it increases. Reduction technique controls the crystallite size and slowly converts to the m- ZrO_2 as calcination temperature increases.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

Zirconium dioxide (ZrO_2), sometimes known as zirconia, is a white crystalline oxide of zirconium (Zr). Zirconia as a pure oxide does not occur in nature but it is found in baddeleyite and zircon ($ZrSiO_4$) which form the main sources for the material. Of the two of these, zircon is by far the most widespread but it is less pure and requires a significant amount of processing to yield zirconia. Pure zirconia exists in the monoclinic form at room temperature. Cubic and tetragonal phases are also stable at higher temperatures. The transformation of monoclinic to cubic zirconia occurs at 800-1000 °C and is accompanied by a large change in lattice size. A consequence of this phase change is a large volume expansion on cooling which make the fabrication of pure zirconia ceramics impossible. In order to manufacture zirconia components, it is necessary to 'lock' the material wholly or partially into the cubic form by the use of additives or stabilising agents. Zirconium dioxide is one of the most studied ceramic materials. Zirconia in its tetragonal stable state has versatile application. It has excellent strength & fracture toughness, so called as 'superplastic' structural ceramic material. It was also postulated that the stabilization of the tetragonal phase at low temperature is due to the lower surface energy of this phase. In recent years there has been an increasing interest in the preparation of ultrafine zirconia powder because of widespread, well documented use of stabilised. Zirconia has density 5.89 g/cm³ and low thermal conductivity. It can be used upto temperature 2400⁰C. It also has very high ionic conductivity and low electronic conductivity.

1.2 Different polymorphs of ZrO_2

Pure ZrO_2 exists in three crystal phases at different temperature. At very high temperature (>2370 °C) the material has cubic structure known as 'cubic zirconia (c- ZrO_2)'. At intermediate temperature (1170 °C to 2370 °C) has tetragonal structure (t- ZrO_2). At low temperature (< 1170 °C) the material transform to the monoclinic structure (m- ZrO_2), which is the most naturally occurring form of ZrO_2 . As mentioned above, ZrO_2 has monoclinic, tetragonal and cubic three polymorphs and distribution of atoms in these three structures are given in Fig. 1.1.

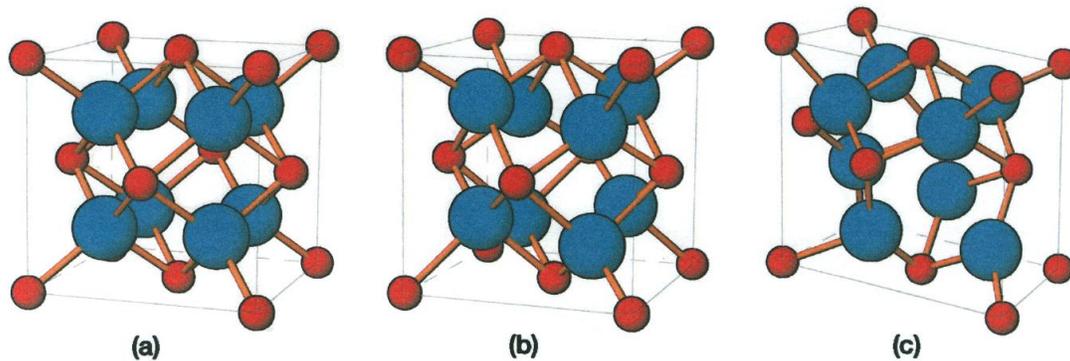


Fig. 1.1: Schematic representations of atomic distributions in ZrO_2 in (a) cubic, (b) tetragonal, and (c) monoclinic crystal structure

The transformation from tetragonal to monoclinic is rapid and accompanied by 3 to 5 percent volume increase that causes extensive cracking in material. This behavior destroys the mechanical property of fabricated component during cooling and makes zirconia useless for any structural application.

1.3 Stabilization of Zirconia

Zirconia is very useful in its 'stabilized' state. In some cases, the tetragonal phase can be metastable. If sufficient quantities of the metastable tetragonal phase is present, then an applied stress, magnified by the stress concentration at a crack tip, can cause the tetragonal phase to convert to monoclinic, with the associated volume expansion. This phase transformation can then put the crack into compression, retarding its growth, and enhancing the fracture toughness. This mechanism is known as transformation toughening, and significantly extends the reliability and lifetime of products made with stabilized ZrO_2 .

It has been found that the high temperature ZrO_2 forms can be stabilized at room temperature by addition of a small amount of oxides as MgO , CaO , Y_2O_3 , CeO_2 etc. Stabilization of t or c - ZrO_2 at low temperature is still a matter of controversy. Garvie developed the following

equation for critical grain size in pure unconstrained ZrO_2 based on surface free energy considerations as given below.

On the basis of the lower value of the surface energy t-phase (γ_t) in relation to m-phase (γ_m), Garvie ^[7] considers that in order to stabilize t- phase at low temperature the following equation must be satisfied:

$$(G_t - G_m) + S_t\gamma_t - S_m\gamma_m \leq 0$$

Where G is the molar free energy and S is the surface area in the single crystal particle. It was determined that particle size for stabilizing t- phase must be ≤ 30 nm.

It is suggested that domain boundaries inhibit $t \rightarrow m$ transition; existence of an active nucleation site and mobility of grain boundaries can be strongly reduced by pores, dopants and particles of a second phase. The most stable polymorphic phase is the one that has the lowest free energy under given conditions (composition, temperature and pressure).

With sufficient amount of additives the high temperature cubic or tetragonal structure can be maintained at room temperature. Cubic or tetragonal stabilized zirconia is a useful ceramic material because it does not go through destructive phase transition during heating and cooling.

1.4 Different synthesis technique to prepare zirconia nanoceramics

In the recent years there has been an increasing interest in preparation of ultrafine zirconia powders because of widespread, well documented use of stabilized zirconia ceramics for both structural and functional applications, as well as development of zirconia toughened ceramics and zirconia ceramic matrix composites. Many methods have been explored to get superfine ZrO_2 powders with surface area and suitable pore size distribution such as sol-gel, thermomechanical attrition, reduction, combustion, glycothermal process, alcohothermal – SCFD (supercritical fluid drying) process, CO_2 supercritical drying, , Hydrothermal processing and precipitation routes. In particular, a chemical solution method, which involves formation of a stable particle by a direct reaction between the atoms or reaction species, provides the most suitable way of synthesizing a sample of imperfection/defect free particles.

1.5 Applications of ZrO₂

- The cubic phase of zirconia also has a very low thermal conductivity which has led to its use as a thermal barrier coating in jet turbine and diesel engine to allow operation at high temperature.
- Stabilized zirconia is used in oxygen sensor and fuel cell membrane because it has the ability to allow oxygen ions to move freely through crystal structure at high temperature. This high ionic conductivity makes it one of the most useful electro-ceramics.
- It is used as a refractory material in insulation, abrasives, enamels and ceramic glazes.
- Zirconia is also an important dielectric material that is being investigated for potential application as an insulator in transistors in future nano-electric devices.
- The tetragonal zirconia has both acidic and basic properties and gives the most active catalyst for some catalytic reactions and higher density of tetragonal zirconia results in higher volume based activity.

CHAPTER 2

LITERATURE REVIEW

2.1 Effect of pH, crystallite size and calcination temperatures on polymorph of ZrO₂

Zirconia powder has become one of the industrially most important ceramic material and also a potential third generation catalyst support. It has three polymorphs: monoclinic, tetragonal, cubic. The high temperature cubic and tetragonal phase can be stabilized at room temperature by incorporating dopant in the lattice, e.g. CaO, MgO and Y₂O₃. Because of its phase transition from tetragonal to monoclinic around 1100-2730⁰c, it is a challenging study with potentially practical applications to prepare stabilized tetragonal zirconia powders at low temperature. Compared with conventional methods, such as sol-gel, hydrothermal, coprecipitation and surfactant templating methods, ultrasound offers a rapid, controllable way to synthesize nanostructure materials with uniform shape. The stabilization of tetragonal phase at low temperature is due to the lower free surface energy of this phase. It was calculated that if the critical particle size limit of 30nm is exceeded, the t-phase transformed to m-phase. There are few reports which are discussed on the synthesis of t- or c-ZrO₂ by varying pH, temperature and synthesis process.

Enhanced phase stability for Tetragonal Zirconia in precipitation synthesis [*N. L. Wu and T. F. Wu, J. Am. Ceramic. Soc., 83, 3225 (2000)*]

Tetragonal ZrO₂ nanocrystallites with or without yttria (3 mol%) doping have been synthesized via a precipitation process in which the hydrous oxide precipitate reacts with hexamethyldisilazane vapour before calcinations. The nanocrystallites are formed and retain a tetragonal structure for hours after calcinations at temperatures of 300⁰-1100⁰C. The enhanced structural metastability has been attributed to the combined effect of suppressed grain growth and reduced surface energy.

Characterization and synthesis of pure ZrO₂ nanopowders via sonochemical method [J. Liang, X. Jiang, G. Liu, Z. Deng, J. Zhuang, F. Li, Y. Li, Mater. Res. Bull., **38**, 161 (2003)]

Pure ZrO₂ nanopowders have been synthesized via sonochemical method, which is a simple and energy efficient way to synthesize inorganic materials. The as synthesized samples (hydrous zirconia, ZrO₂.nH₂O) are characterized by several techniques: XRD, thermogravimetric analysis, photoluminescence spectrometer and Raman spectrometer. It is shown that t-ZrO₂ sample has two photoluminescence bands corresponding to the wavelength of excitations of 254 and 412nm. It is also from XRD result that the transition to the crystalline tetragonal and then to monoclinic form occur as the temperature increased between 300 °C and 1200°C.

Effect of thermal treatment on the crystal structure and morphology of zirconia nanopowders produced by three different routes [M. M. Rashad, H. M. Baioumy, J. Mater. Process. Techno., **195**, 178 (2008)]

Zirconia ZrO₂ nanopowders have been successfully prepared via three processing routes, namely, conventional precipitation (CP), citrate gel combustion (CGC) and microemulsion refined precipitation (MRP). The formed zirconia particles were characterized using X-ray diffraction analysis (XRD), scanning electron microscope (SEM), Fourier transformer infrared (FT-IR) spectroscopy and UV–visible absorption spectrum. The results showed that the CP route led to the formation of tetragonal ZrO₂ phase with low crystallinity at 700 °C and the formed tetragonal phase was transformed to monoclinic ZrO₂ phase at temperatures ranged from 1000 °C to 1200°C. The CGC route led to formation of monoclinic phase without presence tetragonal phase species in the temperatures range from 1000 °C to 1200 °C. In contrast, MRP technique led to the formation of tetragonal phase with high crystallinity compared with the other processing at 700°C and the produced tetragonal phase was inverted to cubic phase by increasing the calcination temperatures from 1000 °C to 1200°C. SEM showed that the morphology of the produced zirconia nanopowders changed according to synthesis routes and thermally treated temperatures.

Improvement in sinterability and phase stability of hydroxyapatite and partially stabilized zirconia composites [Z. Evis, M. Usta, I. Kutbay, J. Euro.Ceram.Soc., **19**, 621(2009)]

Composites of hydroxyapatite with partially stabilized zirconia with MgO or MgF₂ were pressureless sintered between 1000 °C and 1300 °C. The reactions and transformations of phases were verified by X-ray diffraction. For the hydroxyapatite and zirconia composites with MgO, calcium from the hydroxyapatite diffused into the zirconia phase, and the hydroxyapatite decomposed to tri-calcium phosphate at sintering temperatures higher than 1000°C. Above about 1200 °C, CaZrO₃ was formed. Composites containing the MgF₂ decomposed slower than the composites with MgO, which was verified by the changes in the lattice volume of the hydroxyapatite left in these composites. Fluorine ions in MgF₂ diffused into hydroxyapatite, which resulted in thermal stability at high sintering temperatures. Composites with MgF₂ had higher hardness than those with MgO. The lowest porosity was found in a composite initially containing 10 wt% partially stabilized zirconia and 5 wt% MgF₂.

Chemical synthesis of stabilized nanocrystalline zirconia powders [J. Indust.Engg. Chem., **12**, 142]

Nanocrystalline metastable phases of zirconia can be prepared through a novel chemical method using a polymer-based precursor solution with sucrose, poly(vinyl alcohol), and metal ions. Pyrolysis of the precursor over a hot plate at ca. 250 °C followed by calcination at temperatures up to 1200 °C resulted in zirconia nanocrystals in the form of a powder. Y³⁺, Cr³⁺, Th⁴⁺, Ta⁵⁺, and Nb⁵⁺ were used as stabilizing agents. Precursors and powders were characterized using TG-DTA, XRD, and TEM. The tetragonal and cubic phases were stabilized and the particle sizes of the powders were 20~60 nm having crystallite sizes 5 ~30 nm.

Hydrothermal Synthesis and Characterization of Zirconia Nanocrystallites [H. Zhu, D. Yang, L. Zhu, J. Amer. Ceram. Soc., **90**, 1334 (2007)]

This work focuses on the synthesis of tetragonal zirconia (ZrO₂) nanocrystallites with diameter of 5nm by hydrothermal process of hydrazine hydrate. Structural characterization of the ZrO₂ products using X-ray diffraction and Raman spectroscopy revealed that the predominant crystal phase was the tetragonal phase. High resolution transmission electron microscopy images

further showed that the diameter of the majority of the tetragonal ZrO₂ nanocrystallites was < 5nm. He discussed the mechanism of hydrothermal process and the critical roles of hydrazine hydrate in the hydrothermal formation of the small-sized ZrO₂ nanocrystallites.

Critical particle size and phase Transformation in Zirconia: Transmission Electron Microscopy and X-ray Diffraction Studies [R. Srinivasan, L. Rice, B. H. Davis, *J. Am. Ceram. Soc.*, **73**, 3528 (1990)]

A study was undertaken to examine the crystallite size effect on the low-temperature transformation of tetragonal zirconia, Zirconia was prepared by precipitation from a solution of zirconium tetrachloride by adding ammonium hydroxide to produce a pH of 2.95. Portions of the sample, after drying, were calcined at 500⁰C for various time intervals. Phase transformation was followed by X-ray diffraction, the data shows that the tetragonal phase was initially formed and it was transformed to the monoclinic phase at longer periods of calcinations. It was observed TEM particle size and XRD crystallite size that the transformation does not appear to be due to a critical particle size effect.

The influence of pH on Zirconia formed from Zirconium (IV) Acetate solution [F. J. Berry, S. J. Skinner, I. M. Bell, R. J. H. Clark, C. B. Ponton, *J. Sol. State Chem.*, **145**, 394 (1999)]

The influence of the pH of the reaction mixture on the nature of zirconia formed from Zirconium (IV) Acetate solution processed either by boiling under reflux or by hydrothermal methods, has been investigated. The resulting gels and powders were calcined in air at various temperatures and characterized by XRD and Raman Spectroscopy. The latter technique was found to be superior in differentiating tetragonal and cubic zirconia. Zirconia formed from solutions at high pH was found to contain a greater quantity of the tetragonal polymorph, suggesting that the addition of alkali to the solution tends to stabilize the tetragonal form against the conversion to the monoclinic form. The high pressure associated with the hydrothermal treatment is important for the direct formation of monoclinic zirconia under acidic condition.

The effect of processing parameters on particle size in ammonia-induced precipitation of zirconyl chloride under industrially relevant conditions [Powder Techno., **191**, 218 (2009)]

The effect of pH of precipitation, starting solution concentration, and agitation levels on the particle size of hydrous zirconia precipitates has been investigated. It was found that all three

variables affect the particle size of the hydrous zirconia. The smallest particle size is produced by a 0.81 M starting solution, precipitated at pH 12 with a high agitation level. The pH of precipitation was also found to have a significant impact on the type of hydrous zirconia produced. TGA/DTA, micro combustion and TEM/EDS were used to investigate the difference in the powders produced at pH 3 and 12. This work suggests that powders produced at pH 3 will have a structure similar to $Zr[OH]_4$ whilst those at pH 12 are more likely $ZrO[OH]_2$. XRD and microcombustion suggest that the powders produced at pH 3 retained ammonium chloride whilst those produced at pH 12 did not. The filtration rates for the pH 3 products were significantly faster than that of the powders made at pH 12 which is significant in the industrial production of these materials.

Synthesis of zirconia nanopowders from various zirconium salts via polyacrylamide gel method [J. Euro. Ceram. Soc., 28, 773 (2008)]

Pure monoclinic zirconia nanopowders were synthesized via a simple, fast and low cost method; polyacrylamide gel method. Also, the effect of initial salt precursor on thermal behavior of gel network and structure of the synthesized nanoparticles was studied with thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The XRD results showed that the presence of nitrate ions not only retarded the crystallization, but also delayed the tetragonal to monoclinic phase transformation of zirconia nanoparticles which resulted in smaller particle sizes in comparison with the chloride samples. However, TG-DTA analysis confirmed accelerator role of nitrate ions on degradation of polymeric network. Thus, it was expected that zirconia nanopowders synthesized by nitrate samples have bigger sizes than the chloride base powders. Therefore, the presence of nitrate ions affects the synthesized nanoparticle size via two different mechanisms: the retarded crystallization and polymeric network degradation. But, TEM images revealed that the controlling mechanism is the former one.

2.2 Summary of literature

TITLE	RESULT	REFERENCE
Enhanced phase stability for tetragonal Zirconia in precipitation Synthesis	Monoclinic phase exists < 400 °C Size of ZrO ₂ crystallite increases as the calcinations temperature increases from 8nm at 400°C to 25nm at 900 °C.	N. L. Wu and T. F. Wu, J. Am. Ceram. Soc., 83 ,3225(2000)
Characterization and synthesis of pure ZrO ₂ nanopowders via sonochemical method.	t-phase seen around 300°C, m-phase observed around 1200°C	J. Liang, X. Jiang, G. Liu, Z. Deng, J. Zhuang, F. Li, Y. Li, Mater. Res. Bull., 38 ,161(2003)
Effect of thermal treatment on crystal structure and morphology of Zirconia nanopowder produced by three different route.	In Conventional geletion t-ZrO ₂ formed at 700 °C with low crystallinity. In CGS route m-ZrO ₂ formed at 1000 °C to 1200 °C. In MRP route t-ZrO ₂ with high crystallinity formed at 700 °C.	M. M. Rashad, H. M Baoumy, J. Mater. Process. Techno., 195 , 178 (2008)
Improvement in sintering and phase stability of hydroxyapatite and partially stabilized Zirconia composites.	t-ZrO ₂ exist at 1000 ⁰ C and m-ZrO ₂ at 1200 ⁰ C.	Z. Evis, M. Usta, I. Kutbay, J. Euro. Ceram. Soc., 19 621 (2009)
Chemical synthesis of stabilized nanocrystalline Zirconia powder.	The tetragonal and cubic phases were stabilized and the particle sizes of the powders were 20~60 nm having crystallite sizes 5 ~30 nm.	J. Indus. Engg. Chem., 12142-148
Hydrothermal synthesis and caharacterization of zirconia nanocrystallites.	It can be found out that small sized t-ZrO ₂ nanocrystallites were prepared by the hydrothermal process using Hydrazine Hydrate as mineralizer at 150 ⁰ C.	H. Zhu, D. Yang, L. Zhu., J. Am. Ceram. Soc., 90 , 1334 (2007)
Critical particle size and phase transformation in zirconia.	t-phase would be stabilized in particle of diameter 30nm or small.	R. Srinivasan, L. Rice, B. H. Davis, J. Am. Ceram. Soc., 73 ,3528 (1990)
Influence of pH on Zirconia formed from Zirconia Acetate Solution	t-phase transformation occur at 500 ⁰ C,partial transformation to m-phase occur at 900 ⁰ C and completes at 1400 ⁰ C.	F. J. Berry, S. J. Skinner, I. M. Bell, R. J. H. Clark, C. B. Ponton, J. Sol. State Chem., 145 ,394 (1999)

Effect of processing parameter on the particle size in ammonia induced precipitation of zirconyl chloride under industrially relevant condition.	Increase in pH produce small particle size, Increase in Zirconyl chloride concentration produced larger particles, Increase in agitation produce smaller particles.	Powder Techno., 191 , 218(2009)
Synthesis of zirconia nanopowders from various zirconium salts via polyacrylamide gel method	At 300 °C zirconia has Amorphus structure. At 400 °C semicrystalline structure, at 600°C both monoclinic and tetragonal phase detected , At 800°C complete transformation to monoclinic phase occurs.	J. Euro. Ceram. Soc., 28 , 773(2008)

Summary of the literature survey are

1. There are different routes for the stabilization of ZrO_2 with or without any stabilizer.
2. Different polymorphs of ZrO_2 are dependant on pH, crystallite size and calcination temperature.
3. High pH of the solution has better stability on t- ZrO_2 as compared to low pH at elevated temperature.
4. Development of monoclinic phase is observed when the tetragonal crystallite of ZrO_2 reaches values close to that of critical crystallite size (~30nm) .
5. As temperature increases, the crysrallite size increases and simultaneously t-phase of ZrO_2 decreases.
6. Stabilization of t-phase most likely due to low surface energy of the t-phase relative to m-phase.
7. Stabilization of tetragonal phase in most cases is upto 500⁰C and monoclinic phase is upto 1000⁰C.

2.3 Objectives of the present studies

The main objectives of the present studies are:

- To synthesis metastable t-ZrO₂ by varying pH through different synthesis conditions such as gelation, precipitation and maintaining at a constant pH using NaBH₄.
- To analyze the stabilization behavior of metastable t-ZrO₂ by varying the synthesis conditions and concentration of NaBH₄.
- Study and compare the thermal, structural, microstructural and IR result of the as prepared ZrO₂ powder calcined at different temperature.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Synthesis

This work reported the preparation of small sized t-ZrO₂ nanocrystallites by reduction of Zr-salt with a reducing agent (NaBH₄) in three different reaction conditions such as gelation, precipitation and maintaining at a constant pH.

Gelation, precipitation and constant pH reaction conditions are one of the important techniques for synthesizing nanosize ceramic material because pH of the reaction mixture has a considerable influence on the nature of zirconia obtained.

Two aqueous solution of 1 M Zr-salt (ZrOCl₂.8H₂O) and NaBH₄ (5M and 0.5M) were prepared from high purity salts. The Zr-salt solution was highly acidic with pH of ~ 0.3. The NaBH₄ solution, which had a highly basic pH of ~ 11, was added drop wise to the Zr- salt solution with continuous stirring using magnetic stirrer at room temperature.

Gelation: In this case, reducing agent was added dropwise to the Zr-salt that leads to increase in pH of the Zr-salt. A uniform white gel was obtained at a pH ~ 2.6. The product was separated out.

Precipitation: In precipitation process, the gel was broken and further addition of reducing agent leads to increase in pH. At a higher pH of around 9.6, precipitates were formed and settled at the bottom of the beaker.

Maintaining at a constant pH: In this case, Zr-salt was added to the reducing agent, which leads to decrease in pH. Hence, the reducing agent NaBH₄ solution was added further to the solution along with Zr-salt to maintain the pH throughout the reaction. In this case, the pH ~ 11 was maintained throughout the reaction.

These three different conditions products were thoroughly washed with hot water (remove NaCl and borate phase) and dried in oven. The fine powders obtained after drying were heat treated at selected temperatures to study the formation and thermal stability of ZrO₂ polymorph and also its phase transformation to equilibrium m-ZrO₂ structure.

3.2 General characterization

3.2.1 Thermal

Thermal decomposition of an amorphous ZrO_2 powder followed by its reconstructive nucleation of t- ZrO_2 nanoparticles were studied using differential scanning calorimetric and thermogravimetric (DSC-TG) by heating the sample at $10\text{ }^\circ\text{C}/\text{min}$ in argon in a thermal analyzer (Netzsch, Germany).

3.2.2 X-ray diffraction

Phase analysis was studied using the room temperature powder X-ray diffraction (Model: PW 1830 diffractometer, Phillips, Netherland) with filtered 0.154056 nm $\text{Cu K}\alpha$ radiation. Samples are scanned in a continuous mode from $20^\circ - 80^\circ$ with a scanning rate of $0.02\text{ (degree)}/1\text{ (sec)}$.

3.2.3 Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the powder is dispersed in isopropyl alcohol in an ultra sonication bath (20 kHz , 500 W) for half an hour. One drop of the well-dispersed sample solution is deposited on to polished brass plate. This brass plate was used for microscopy.

3.2.4 Particle size measurement:

Size of the particle is usually obtained with the help of scanning electron microscopy (SEM). The size corresponds to the mean value of the crystalline domain size of the particles is determined from the X-ray line broadening using Debye-Scherrer formula with correction factor as given below.

$$D = 0.9 \lambda / \beta \cos\theta \quad \text{Where } \beta = \sqrt{(\beta_{\text{sample}}^2 - \beta_{\text{standard}}^2)}$$

Where D is average crystalline size, λ is the wavelength used, β the angular line width of half maximum intensity and θ is the Bragg's angle in degree. Standard value of β is taken as the angular line width of half maximum intensity for polycrystalline SiO_2 material.

3.2.5 IR-Spectroscopy:

IR spectra of the powders in KBr pellets were studied in the range of $400 - 4000\text{ cm}^{-1}$ by using IR-spectrometer.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes thermal, structural, microstructural and infra-red analysis of ZrO_2 nanoparticles prepared through gelation, precipitation and reduction at constant pH process using $NaBH_4$.

4.1 Thermal behavior of as-prepared ZrO_2

Fig. 4.1 and Fig. 4.2 show the DSC-TG graphs of gelation and constant pH as-prepared powder synthesized using 5 M $NaBH_4$. In the DSC plot there was an endothermic peak at ~ 150 °C is due to desorption of absorbed water on the surface of ZrO_2 powders. The total weight loss upto 1000 °C for gelation and constant pH ZrO_2 powder was found to be around 26 % and 22 % respectively. The crystallization peak of t- ZrO_2 from a- ZrO_2 was observed at 600 °C for gelation and 800 °C for constant pH process. Below these temperatures, the nature of zirconia was found to be an amorphous that was confirmed through XRD pattern.

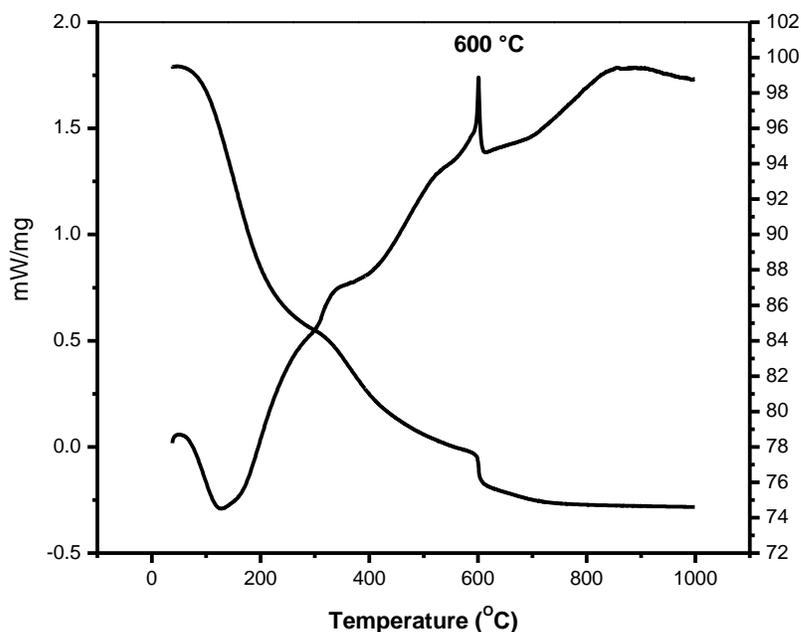


Fig. 4.1 shows the DSC-TG graphs of as-prepared ZrO_2 synthesized through gelation process

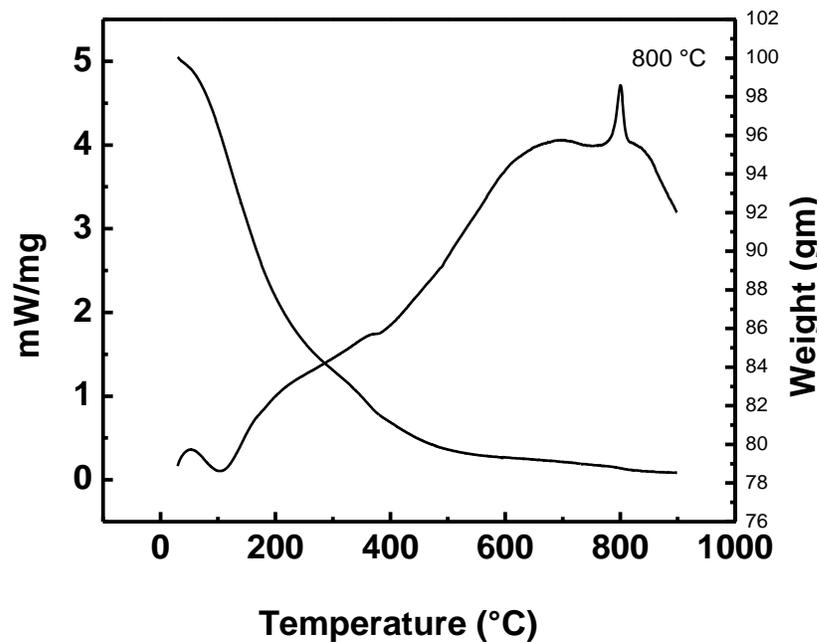


Fig. 4.2 shows the DSC-TG graphs of as-prepared ZrO_2 synthesized through constant pH process

4.2 Structure and microstructure

The presence of various phases and crystallite size were determined from the X-ray diffraction pattern. Fig 4.2 shows the XRD patterns of calcined ($600\text{ }^\circ\text{C}$) ZrO_2 powder synthesized using different concentration of $NaBH_4$ (5M and 0.5M). XRD of powder obtained using 5M and 0.5M $NaBH_4$ by the gelation and precipitation process shows the complete development of tetragonal phase, Whereas in reduction at constant pH process at both the concentration shows amorphous behavior .

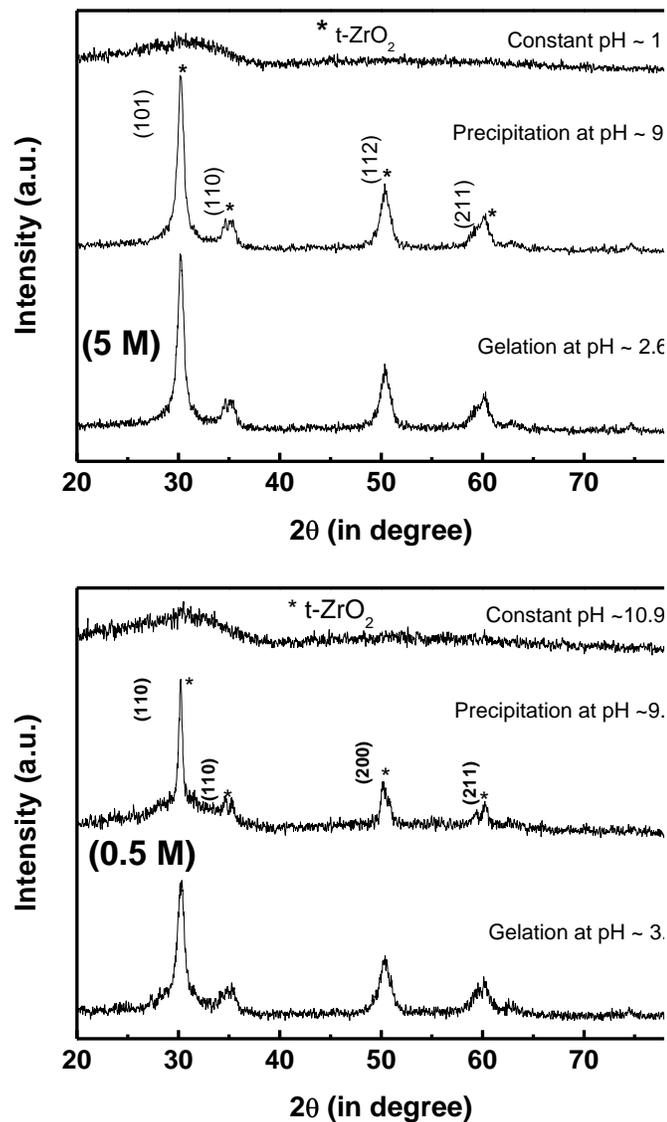


Fig. 4.3: X-ray diffraction pattern of calcined (600 °C) ZrO_2 powder synthesized using different concentration of $NaBH_4$.

Here Fig. 4.3: shows X-ray diffraction pattern of calcined (800 °C) ZrO_2 powder synthesized using different concentration of $NaBH_4$ (5M, 0.5M). XRD pattern of ZrO_2 powder obtained from the Gelation and precipitation process using 5M $NaBH_4$ shows complete transformation of tetragonal phase to monoclinic, whereas in case of 0.5M $NaBH_4$ gelation process shows monoclinic phase with a small development of tetragonal phase. In case of

precipitation process using 5M NaBH₄ shows complete monoclinic phase whereas in 0.5M NaBH₄ shows a mixture of monoclinic and tetragonal phase. Whereas in case of powder obtained from reduction at constant pH using both the concentration of NaBH₄ shows only tetragonal Zirconia having crystallite size about 25 nm.

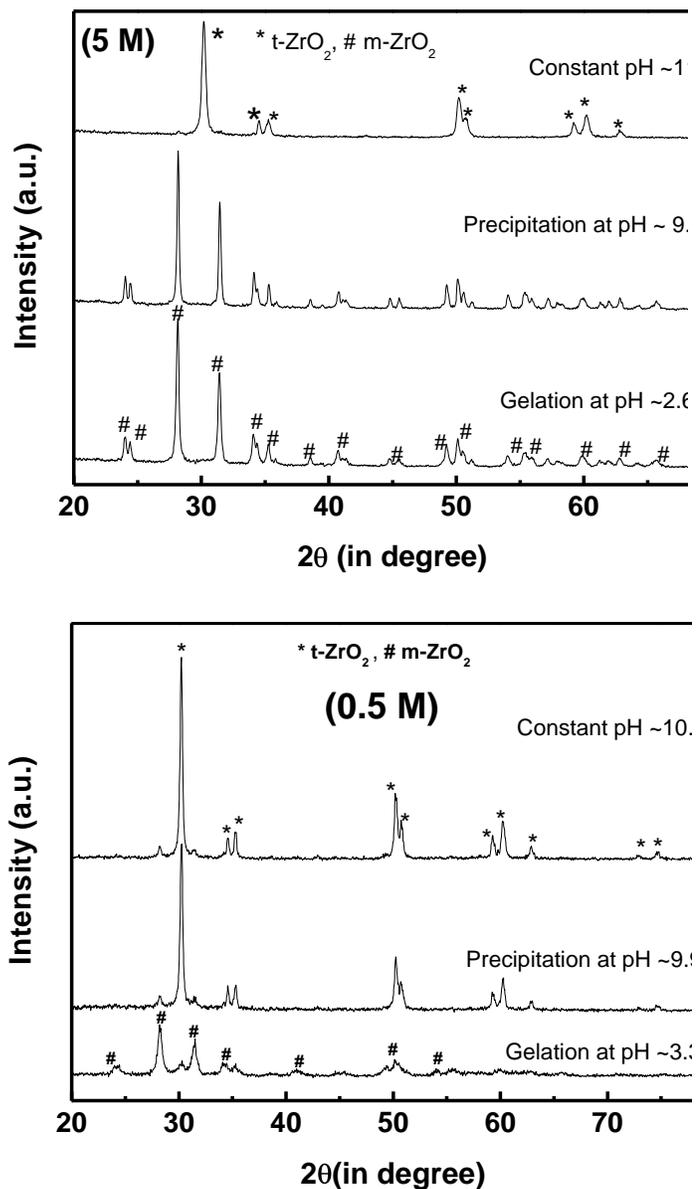


Fig. 4.4: X-ray diffraction pattern of calcined (800 °C) ZrO₂ powder synthesized using different concentration of NaBH₄.

Indexing of planes :

m-ZrO₂
JCPDS File name : PDF# 830944

2θ	D spacing	Intensity	h k l
28.219	3.1598	999	111
31.503	2.8375	670	111
50.192	1.8161	208	220
24.086	3.6919	158	011
50.638	1.8012	118	122
24.487	3.6323	117	110
41.455	2.1764	46	121

t-ZrO₂
JCPDS File Name : PDF#91771

2θ	D spacing	Intensity	h k l
30.259	2.9513	999	101
50.281	1.8131	326	112
60.272	1.5341	212	211
50.801	1.7958	172	200
34.611	2.5895	80	002
62.933	1.4756	51	202

Table 4.1: Indexing of different planes of Zirconia samples reduced at various concentration of NaBH₄ calcined at 600⁰C and 800⁰C .

Crystallite size of the Zirconia Nanoparticles:

For 0.5M NaBH₄:

Synthesis process	Temperature	Crystallite size in (nm)	Major Phase	Minor phase
Gelation at pH-3.3	600 ⁰ C	11	Tetragonal	No
	800 ⁰ C	19	Monoclinic	Tetragonal
Precipitation at pH-9.9	600 ⁰ C	20	Tetragonal	No
	800 ⁰ C	23	Tetragonal	Monoclinic
Reduction at constant pH-10.9	600 ⁰ C	-	Amorphous	No
	800 ⁰ C	25	Tetragonal	No

For 5M NaBH₄:

Synthesis process	Temperature	Crystallite size in (nm)	Major phase	Minor phase
Gelation at pH-2.6	600 ⁰ C	13	Tetragonal	No
	800 ⁰ C	38	Monoclinic	No
Precipitation at pH-9.6	600 ⁰ C	11	Tetragonal	No
	800 ⁰ C	37	Monoclinic	No
Reduction at constant pH-11	600 ⁰ C	-	Amorphous	No
	800 ⁰ C	25	Tetragonal	No

Table 4.2: Crystallite size and phase composition of heat-treated (600 °C, 800⁰C) ZrO₂ prepared by three different route gelation , precipitation and reduction at constant pH at different concentrations of NaBH₄

SEM gives the information about size, shape and morphology of the ZrO₂ .Fig. 4.3 shows SEM micrographs of calcined (600 °C) ZrO₂ powders synthesized through (a) gelation (b) precipitation and (c) constant pH process. SEM images of powder prepared by gelation process shows dendritic structure, where particles are arranged in a long chain. Whereas in case of powder prepared by precipitation and reduction at constant pH, the SEM image shows particles are agglomerate at nm dimension.

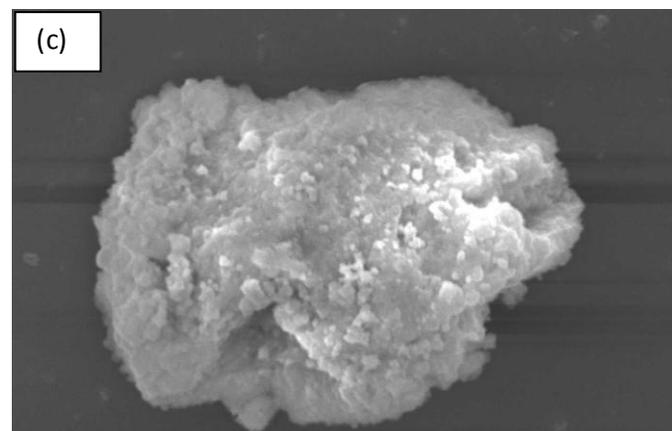
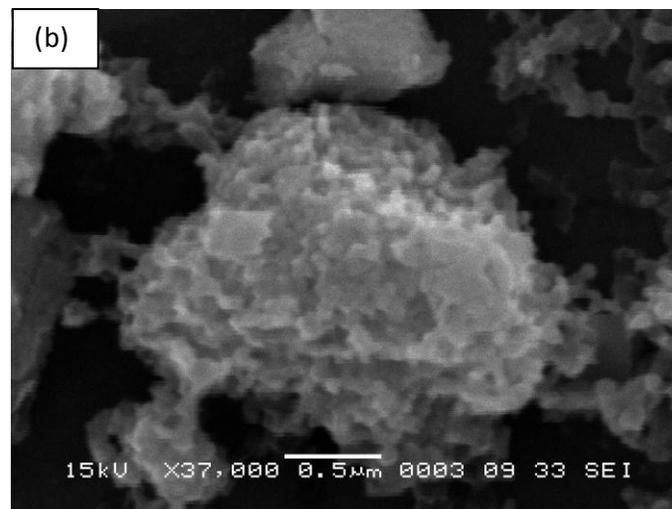
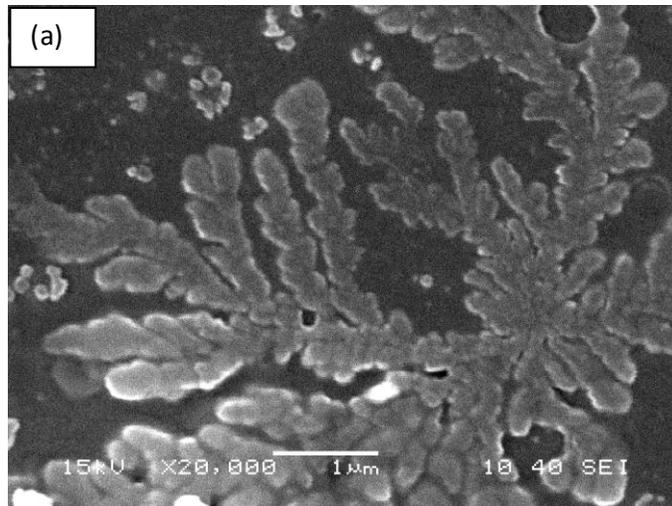


Fig. 4.5: SEM micrographs of calcined (600 °C) ZrO_2 powders synthesized through (a) gelation (b) precipitation and (c) constant pH process.

4.3 IR spectra of as-prepared ZrO₂ powders

Infra-Red spectra in the range of 400 – 4000 cm⁻¹ for as-prepared ZrO₂ powders synthesized using NaBH₄ was shown in Fig. 4.4. Individual bands of the Zr-O group vibrations exist in both ZrO₂.xH₂O and ZrO₂. Also O-H bending and stretching vibrations exist in ZrO₂.xH₂O and H₂O molecule. The OH group is distinguished easily in H₂O molecule by its bending vibration which appears in a single band at ~1630 cm⁻¹ that confirms the presence of water in the as-prepared powder. Another O-H bending vibrations in the hydroxyl group in the ZrO₂.xH₂O molecule appears at ~ 1360 cm⁻¹ and one asymmetric O-H stretching band occurs in H₂O in the range of 2856 to 3404 cm⁻¹. From the IR spectra, the as-prepared powders reveal that the ZrO₂ nano powders have significant amount of surface-adsorbed H₂O molecules. A weak band at 1195 cm⁻¹ is assigned to B-O asymmetric stretching vibrations from borate groups in the as-prepared ZrO₂ powder. Also two weak bands at 1117 cm⁻¹ and 1029 cm⁻¹ assigned to B-O stretching vibrations from borate groups. Hence, the as-prepared ZrO₂ powder contains small amount of borate phase which could not be detected from XRD. The infrared characteristics bands observed in the as-prepared ZrO₂ nanopowders prepared through NaBH₄ are given in Table 4.3.

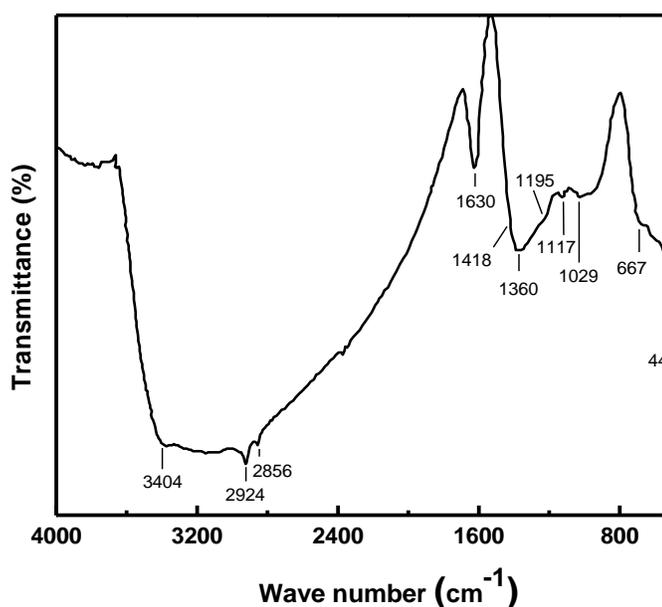


Fig. 4.6: IR spectra of as-prepared ZrO₂ powder synthesized from sodium borohydride

Table 4.3: Infrared characteristic bands observed in as-prepared ZrO₂ nanopowders

Band Position (cm ⁻¹) Reaction with NaBH ₄	Remarks
3404	O-H stretching in ZrO(OH) ₂ .xH ₂ O
2924	or
2856	adsorbed water
1630	O-H bending in H ₂ O
1418	O-H bending in ZrO(OH) ₂
1360	asymmetric O-H stretching
1195	B-O asymmetric stretching
1117	B-O stretching
1029	B-O stretching
667	Zr-O vibration
440	Zr-O vibration

CONCLUSIONS:

The present work deals with the synthesis and enhancement of metastable tetragonal zirconia nanocrystals through three different chemical route. ZrO₂ powder were synthesized through reduction technique by using strong reducing agent (NaBH₄) . The significant finding of this work are,

- From XRD results we conclude that temperature, concentration of reducing agent and pH are vital factor for phase development.
- Stabilization of metastable tetragonal zirconia observed upto 600⁰C for sample obtained by gelation and precipitation technique.
- In case of sample obtained by reduction at constant pH found to be pure amorphous, whereas at 800⁰C fully t-ZrO₂ is seen.
- A mixture of t-ZrO₂ and m-ZrO₂ observed at 800⁰C for the sample prepared by both gelation and precipitation technique.
- At low concentration the crystallite size increases with increase in pH, whereas at high concentration the crystallite size decreases with increase in pH.

- From XRD result it has been concluded that small crystallites (< 25nm) stabilizes metastable t-ZrO₂ upto moderate temperature.
- The as prepared powders contain lots of water in the form of ZrO(OH)₂.xH₂O as studied from IR analysis.
- Reduction technique control the crystallite size and slowly converts to m-ZrO₂ as calcination temperature increases.
- From thermal as well as microstructural studies it was concluded that the stabilization of metastable t-ZrO₂ is dependent on the initial pH of the precursor , calcination temperature and also the crystallite size of the ZrO₂ .

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