

Synthesis, Characterization and Catalytic application of Barium modified Zirconia nanoparticle for the synthesis of β -Nitro alcohols

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This is to certify that the dissertation entitled “**Synthesis, Characterization and Catalytic application of Barium modified Zirconia nanoparticle for the synthesis of β -Nitro alcohols**” being submitted by **Kumari Swarnima & manjulata Hess** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by them under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

N.I.T. Rourkela.

Date:

Dr. Braja Gopal Mishra

Supervisor

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**Kumari Swarnima
Manjulata Hess**

To
OUR PARENTS
WHO ENCOURAGE US
TO PROCEED
AT EVERY STEP
AT EVERY MOMENT
THROUGH
OUR LIFE
TO SOAR HIGHER

CHAPTER 1

INTRODUCTION

The search of recyclable solid heterogeneous base catalysts remains a major challenge in the present day catalysis research. Most of the industrial catalyzed reactions still utilize homogeneous NaOH, KOH, sodium ethoxide and potassium tertiary butoxides as catalysts. These classical catalysts show undisputable advantages in terms easy preparation, low cost and higher activity compared to their heterogeneous counterparts. However, the utility of these catalysts is severely limited by their extreme reactivity, difficulty in separation and recovery and environmental pollution related to their disposal [1]. In recent years there has been effort to replace these classical catalysts by nanosize heterogeneous base catalysts. Few notable heterogeneous catalysts which have been used for base catalyzed reactions are nano CaO, MgO and layered double hydroxides. Calcium oxide based heterogeneous catalysts have been found to be active for several base catalyzed reactions. However, the surface passivation and instability of the active sites by adsorption of CO₂ and H₂O have been found to be a deterring factor for their utility in large scale. MgO on the other hand although display stable surface activity, the high surface energy of the MgO nanocrystals often leads to agglomeration of the particles with consequent loss in surface area and active sites. In recent years, there has been extensive effort to develop novel heterogeneous base materials having activity closer to these homogeneous classical catalysts. Two approaches have been mainly used. The stability of active sites on the surface of these alkali metal and alkaline earth metal has been increased by forming nanocomposite oxides [2]. The formation of nanocomposite oxides has also been found to preserve the surface area. The other approach has been to graft covalently basic organic moieties on the surface of siliceous porous materials with large surface area [3]. The former approach is

more economic and feasible from industrial point of view. Zirconia nanoparticles when synthesized in hydrous form contain a significant fraction of reactive hydroxyl groups on its surface. These hydroxyl groups can act as anchoring sites for catalytically active species. Recently, Essayem et al have synthesized Cs⁺ exchanged zirconia nanoparticles by ion exchange method. The Cs⁺ ions are bonded to the surface of zirconia by electrostatic forces and serve as excellent basic sites due to charge isolation. The heat of adsorption experiment of acidic CO₂ probe indicate that the Cs⁺ exchanged nanozirconia display stronger and thermally stable active sites compared to LDH and MgO [4]. Recent studies on ZrO₂-CaO nanocomposite oxides indicate that these materials contain strong surface basic sites which are thermally stable and capable of catalyzing a variety of organic transformation [2,4]. In ZrO₂-CaO nanocomposite oxide the Ca²⁺ ions substitute Zr⁴⁺ ions in the zirconia lattice to form a substitutional solid solution. The presence of Ca ions introduces oxygen ion vacancy and increases the ionicity of the zirconia crystal resulting in formation of new basic sites [4]. The basicity of the catalyst can be tailored by varying Ca/Zr ratio and adopting proper synthetic procedure. The CaO-ZrO₂ materials have been used as efficient catalyst for selective dehydration reactions, Meerwein-Ponndorf-Verley reduction, autothermal reforming of CH₄ [2, 5]. ZrO₂-MgO nanocomposite oxides comprise another interest class of solid base catalyst. The presence of MgO stabilizes the tetragonal phase of zirconia and helps creating new basic sites in the host zirconia lattice which are resistant to deactivation by hydrolysis. The MgO-ZrO₂ materials have been used as catalyst for aldol Condensation, propylene glycol methyl ether, dimethyl carbonate synthesis, carbon dioxide reforming of methane and glycerol reforming [6,7]. Gong et al have synthesized sodium modified mesoporous zirconia by hard templating approach. Mesoporous silica was used as a template for synthesis of mesoporous zirconia by insitu precipitation. The sodium-modified

mesoporous zirconia exhibit well-defined mesostructure, tetragonal crystalline frameworks, and superbasicity with a high strength of 27.0 in Hammett scale. The sodium-modified mesoporous zirconia exhibit excellent catalytic activity for synthesis of dimethyl carbonate with a turnover number higher than the classical sodium methoxide base catalyst [8]. The literature review clearly indicates that alkali modified zirconia is promising materials for application as heterogeneous base catalyst. It will be interesting to investigate the physicochemical properties of these materials in nanoregime and their subsequent application for base catalyzed organic synthesis involving biologically important molecules.

In the present investigation, we have studied the surface modification of zirconia nanoparticles by barium ion exchange and studied their catalytic application for synthesis of β -nitro alcohol by condensation of nitromethane with aromatic aldehydes. In order to study the effect of the nature of the surface sites and surface area, we have synthesized the zirconia nanoparticles by using different preparation strategies. The following section gives a brief overview of the different methods employed for the synthesis of zirconia nanoparticles.

1.9 Objective of the present study

The main objectives of the present study is

1. Synthesis of zirconia nanoparticles with surface functionality using different preparation methods.
2. Surface modification of the synthesized zirconia nanoparticles by ion exchange with Ba^{2+} ions in order to introduce intrinsic basicity on the surface.

3. Characterization of the synthesized materials by using various analytical techniques such as XRD, IR, FESEM, UV-Vis to obtain complete information on the physicochemical characteristics of these materials
4. Evaluation of the surface parameters and catalytic activity of the of the Barium modified nanozirconia (Ba/ZrO_2) for the synthesis of β -nirtoalcohols by condensation of nitromethane with aromatic aldehydes.

CHAPTER 2

MATERIALS AND METHODS

2.1 PREPARATION OF BARIUM EXCHANGED ZIRCONIA PARTICLES

2.1.1 Preparation of zirconia

The zirconia particles were synthesized by using five different methods namely precipitation using ammonia, urea hydrolysis, amorphous citrate process, combustion method and evaporation induced self-assembly (EISA) in mesoporous form. The precursor salts (zirconyl chloride and zirconyl nitrate), liquid ammonia, urea, citric acid, were procured from Merck India limited. The triblock polymer Pluronic P 123 was used in the EISA method was procured from Sigma-Aldrich limited. Double distilled water prepared in the laboratory was used in all preparation methods. The following sections describes the preparation procedures used in this study for the synthesis of zirconia.

Precipitation method (ZrO₂-P): 200 ml of double distilled water was adjusted to pH 9.5 by addition of liquid ammonia. To this solution required amount of zirconyl chloride solution (3.22 gm in 75 mL of water) was added dropwise (20 ml/h) under constant stirring. The pH of the solution was continuously monitored and maintained at the same pH by drop wise addition of ammonia solution. After the completion of the precipitation process, the aqueous mixture was allowed to stir for 6 h followed by multiple washing in double distilled water (till Cl⁻ free). The precipitated materials were recovered by filtration and then dried at 120°C for 12 h in hot air oven and calcined at 450°C for 2 h to obtain the zirconia particles.

Amorphous citrate method (ZrO₂-A): A solid mixture containing equimolar amount of zirconyl nitrate and citric acid was dissolved in minimum amount of water at 70°C to form a

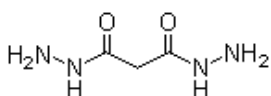
thick transparent paste. The paste was then evacuated at the same temperature until it formed an expanded spongy solid material. This material is immediately transferred to a hot air oven preheated at 160°C. The spongy material was highly hygroscopic and special care was taken while transferring it to the hot air oven. The temperature of the oven was maintained at 160°C for 2 h to decompose the nitrates which yield the amorphous citrate precursor. The amorphous precursor was then calcined at 500°C for 3 h to the zirconia particles.

Urea Hydrolysis (ZrO₂-U): A 200 mL 0.2 M ZrOCl₂ solution was mixed with equimolar amount of urea solution and the resulting mixed solution was refluxed for 12 h at 100°C. The resulting particles were filtered and washed repeatedly with hot water (4-6 times). The precipitate was subsequently dried at 120°C for 12 h in hot air oven and calcined at 500°C for 2 h to obtain the zirconia particles.

Combustion method (ZrO₂-C): The zirconia nanoparticles were synthesized using combustion method using zirconyl nitrate as oxidizer and malonic acid dihydrazide as fuel. The physical and chemical characteristics and the synthesis procedure of malonic acid dihydrazide is given below.

Physical and chemical characteristics of Malonic acid dihydrazide (MDH)

Molecular structure:



Molecular Formula: C₃H₈N₄O₂

Molecular Weight: 132.12

Melting Point: 152-154°C

Synthesis procedure: In a 1000 ml round bottom flask fitted with a reflux condenser, 25.04 g of hydrazine hydrate (0.5 mol) is added dropwise to 40.05g of diethyl malonate (0.25mol) dissolved in 350 ml absolute ethanol. The mixture is refluxed for five hours. The clear solution obtained is

cooled and then concentrated to half of its volume. The concentrate is kept overnight at room temperature to obtain white crystals of Malonic acid dihydrazide which are filtered and dried.

In a typical combustion synthesis procedure for the preparation of zirconia at a reaction stoichiometry of F/O =1 using MDH as fuel, 1.42 g of zirconium oxynitrate was mixed with 0.99 g of MDH fuel and dissolved in minimum amount of water to obtain a redox mixture. The redox mixture was kept in a muffle furnace preheated at 400°C. The redox mixture was found to get instantaneously ignited releasing a lot of gaseous products. The combustion residue is subsequently cooled, grinded and calcined at 500°C in air for 2h to obtain the zirconia particles.

Evaporation induced self-assembly method (ZrO₂-E): Zirconia in mesoporous form was synthesized using evaporation induced self-assembly method using Pluronic P 123 as structure directing agent. In a typical procedure, 1 mL of Pluronic P 123 was dissolved in 30 mL ethanol by stirring at room temperature for 2 h. To this solution 3.75 gm of zirconyl nitrate was added and stirred for 2 h. Special care was taken not to lose ethanol during the stirring process. The resulting solution was then heated at 80°C in an oil bath till the ethanol was evaporated. The oil bath temperature was reduced to 40°C and kept at that temperature for 24 h. After complete removal of ethanol, the ensuing solid was kept at 100°C for 12 h in a hot air oven which was subsequently calcined at 500°C for 6 h to obtain the ZrO₂-E material.

2.1.2 Preparation of Ba²⁺ ion exchanged zirconia (Ba/ZrO₂): The zirconia particles described in section 2.1.1 (ZrO₂-P, ZrO₂-A, ZrO₂-C, ZrO₂-U and ZrO₂-E) were used for the ion exchange process for synthesis of barium exchanged zirconia (Ba/ZrO₂). In a typical procedure, 4 gm of zirconia was dispersed in a 70 mL of 20 millimolar solution of barium carbonate. The resulting suspension was stirred for 2 h, filtered, dried at 110°C for 6 h and calcined at 550°C for 2 h. The

obtained material was refluxed in 50 mL ethanol for 4 h and dried overnight at 120°C to generate the Ba/ZrO₂ material.

2.2 CHARACTERIZATION OF CATALYST MATERIALS

The materials synthesized in section 2.1 were characterized by X-Ray diffraction (XRD), Field Emission Scanning Electron Microscopy-Energy dispersive X-ray Analysis (SEM-EDAX), UV-Visible spectroscopy (UV-Vis) and Infra Red Spectroscopy (IR).

X-ray diffraction

The X-ray diffraction patterns of the ZrO₂ and Ba/ZrO₂ samples were recorded on a Ultima IV, Rigaku diffractometer using Ni-filtered CuK_α radiation. The XRD measurements were carried out in the 2θ range of 20-70° with a scan speed of 2 degrees per minute using Bragg-Brantano configuration.

Scanning Electron Microscopy

The FESEM analysis was carried out by using Nova NanoSEM/FEI microscope. Prior to FESEM analysis the powder sample is placed on carbon tape followed by carbon coating.

UV-Vis Spectroscopy

UV-Vis Spectra of pure ZrO₂ as well as Ba/ZrO₂ materials were recorded using barium sulphate as reference compound on a Shimadzu spectrophotometer (UV-2450) in the range of 200-900 nm.

Infrared Spectroscopy:

The IR spectra of different zirconia and Ba/ZrO₂ (as KBr pellets) were recorded using a Perkin-Elmer infrared spectrometer with a resolution of 4 cm⁻¹, in the range of 400 cm⁻¹ to 4000 cm⁻¹. Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into

pallets. The pallets were stored in vacuum desiccators and exposed to IR lamp for 1 minute prior to the IR measurement.

2.3 Catalytic studies for synthesis of β -Nitro alcohols by Henry reaction

In a 25 ml round bottom flask, stoichiometric quantity of p-nitrobenzaldehyde (1 mmol), nitromethane (2 mmol) and 50 mg catalyst (Ba/ZrO₂) in 5ml of ethanol was stirred at different temperature for the specified time. After completion of the reaction as indicated by TLC, the reaction mixture was extracted with ethyl acetate (3x5 mL). The organic phase was dried using Na₂SO₄, filtered, and excess ethyl acetate was distilled off in vacuo. Filtration of both organic and aqueous phases led to the recovery of the catalyst.

CHAPTER 3

RESULT AND DISCUSSION

3.1 XRD study

Figure 3.1 and 3.2 shows the XRD patterns of zirconia materials synthesized using different preparation procedures. All zirconia materials show well defined and intense peaks with d values of 3.16, 2.95, 2.85, 2.56, 1.81 and 1.53 Å. These peaks correspond to the presence of both monoclinic and tetragonal phase of zirconia [9].

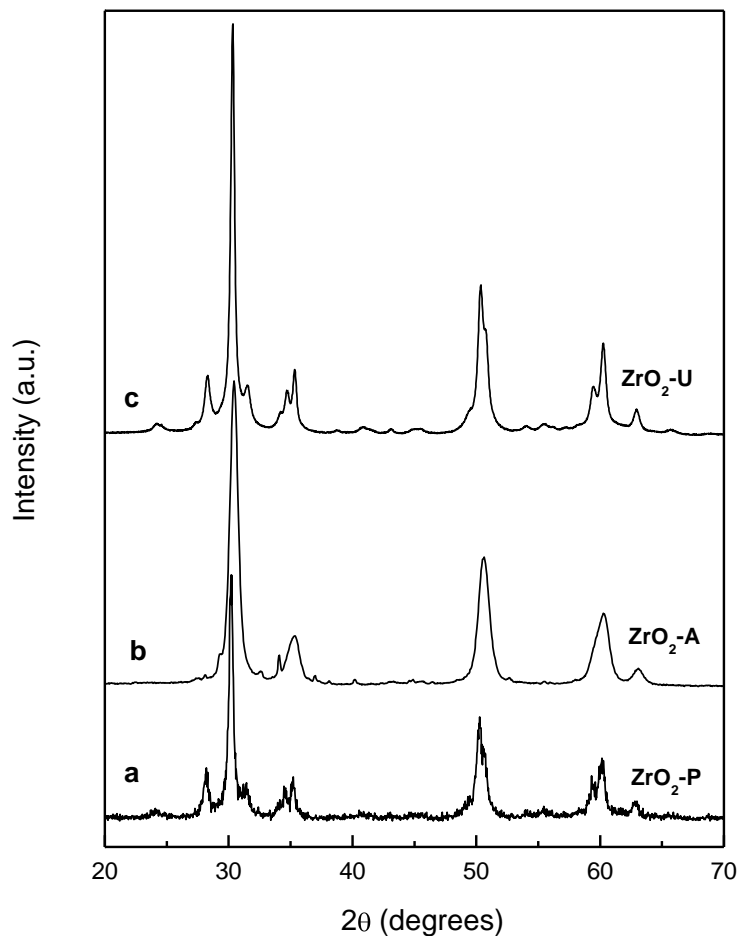


Figure 3.1 XRD patterns of (a) ZrO₂-P, (b) ZrO₂-A and (c) ZrO₂-U.

The relative percentage of the monoclinic and tetragonal phase was found to vary from sample to sample and strongly depends on the preparation procedure adopted. Table 3.1 shows the percentage tetragonal phase present in different zirconia samples calculated using the formula

$$\% \text{ Tetragonal} = \frac{IT(2\theta=30.2)}{IT(2\theta=30.2) + \frac{IM(2\theta=28.2) + IM(2\theta=31.4)}{2}} \times 100 \quad \text{----- (1)}$$

Where IT and IM stands for the integral intensity of the XRD peaks at the specified 2θ values for the tetragonal and monoclinic phases, respectively.

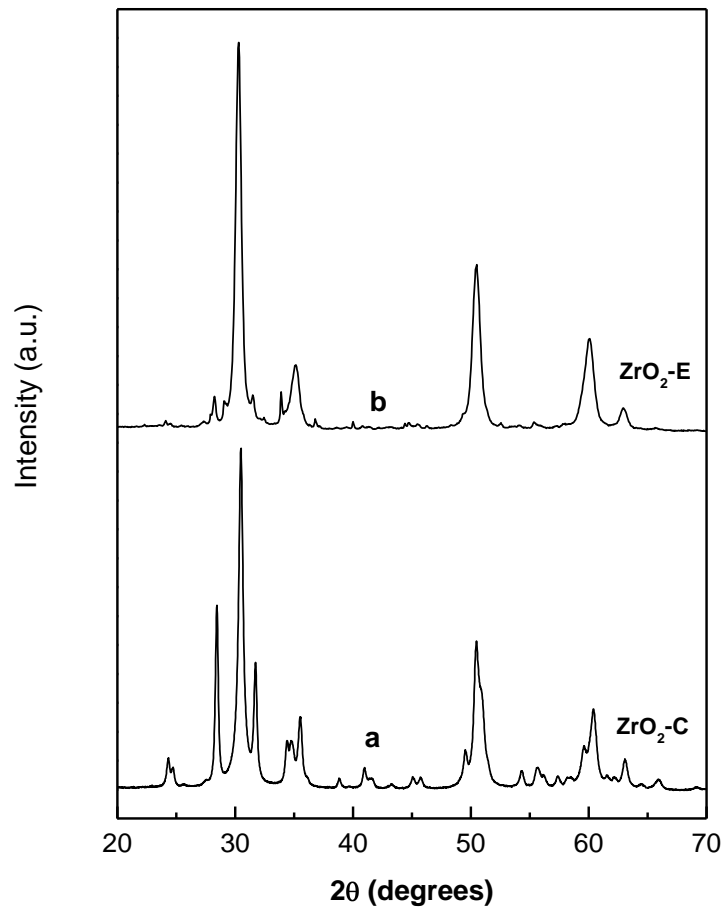


Figure 3.2 XRD patterns of (a) ZrO_2 -C and (b) ZrO_2 -E.

The amorphous citrate process yields zirconia nanoparticles containing predominantly tetragonal phase of zirconia. The combustion method where MDH was used as fuel contains 68.8% tetragonal zirconia.

Table 1. Percentage tetragonal phase and crystallite size of the zirconia and Ba/ZrO₂ materials

SI No	Catalyst	% tetragonal phase	Crystallite size (nm)
1	ZrO ₂ -P	82.9	38.0
2	ZrO ₂ -U	78.3	19.2
3	ZrO ₂ -A	95.5	14.4
4	ZrO ₂ -C	68.8	28.2
5	ZrO ₂ -E	91.7	41.5
6	Ba/ZrO ₂ -P	87.8	45.0
7	Ba/ZrO ₂ -U	57.5	21.5
8	Ba/ZrO ₂ -A	86.1	15.6
9	Ba/ZrO ₂ -C	61.9	32.3
10	Ba/ZrO ₂ -E	84.1	51.6

The selective formation of the tetragonal phase has been a subject of intense study in literature. Srinivasan et al. has reported that in sulfated zirconia catalyst the tetragonal phase is stabilized due to the preferential segregation of the sulfate ions along the grain boundary [10]. The presence of sulfate ions reduces the grain boundary area which prevents the mobility of the ions during phase transformation. It has also been reported that there is a critical crystallite size of zirconia below which the tetragonal phase is stabilized [11]. In the present study, it is believed that the crystallite size reduction is the primary cause of stabilization of the tetragonal phase of zirconia. As the crystallite size decreases, the motion of dislocation in the crystal are severely restricted which prevents the phase transformation of the tetragonal phase to the thermodynamically stable monoclinic phase. The crystallite size are calculated from the Fourier line shape analysis for all samples following the Warren and Averbach method [12] using software BRAEDTH. The peak position (2 θ), full width at half maximum (FWHM) and intensity

are calculated using commercially available software (PEAK FIT) for each peak of the XRD data. The indexing of all peaks of XRD patterns are carried out using 2θ and intensity value of each peak by a standard computer software POWD. The calculated volume-weighted distributions, (pV) as function of the Fourier length (L) for two representative zirconia samples is given in Fig. 3.3. The wide distribution function observed for the ZrO_2 -C sample indicates that the particles are polycrystalline with larger particle size as compared to the ZrO_2 -A sample. The crystallite size calculated from the Fourier line profile analysis is presented in Table 3.1. The zirconia sample synthesized using amorphous citrate process display smaller particle size as compared to the other samples. The Zr-P which is prepared by base hydrolysis of zirconium salt precursor using ammonia as hydrolyzing agent shows larger crystallite size.

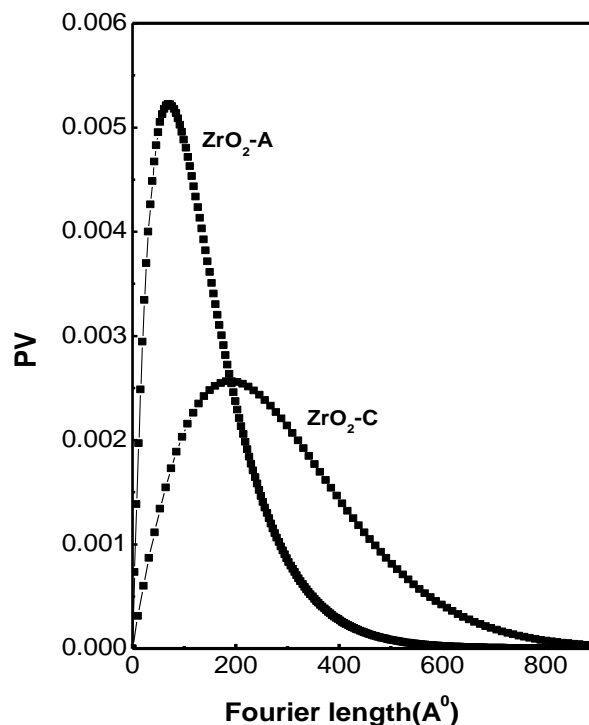


Figure 3.3 Fourier line profile analysis of ZrO_2 -A and ZrO_2 -C material.

The XRD patterns of different Ba/ZrO₂ samples are presented in figure 3.4 and figure 3.5. The Ba stabilized zirconia contains predominantly tetragonal phase of zirconia except in case of Ba/ZrO₂-U and Ba/ZrO₂-C samples. In addition to the tetragonal phase of zirconia, the presence of BaZrO₃ and BaCO₃ are detected in the samples. During heat treatment at 550°C it is likely that some of the surface barium reacted with the zirconia support to form the BaZrO₃ perovskite phase which is apparent from the XRD patterns of the Ba/ZrO₂ samples. The formation of BaCO₃ phase is due to the reaction of the atmospheric carbon dioxide with the BaO phase which is formed as an intermediate phase during heat treatment.

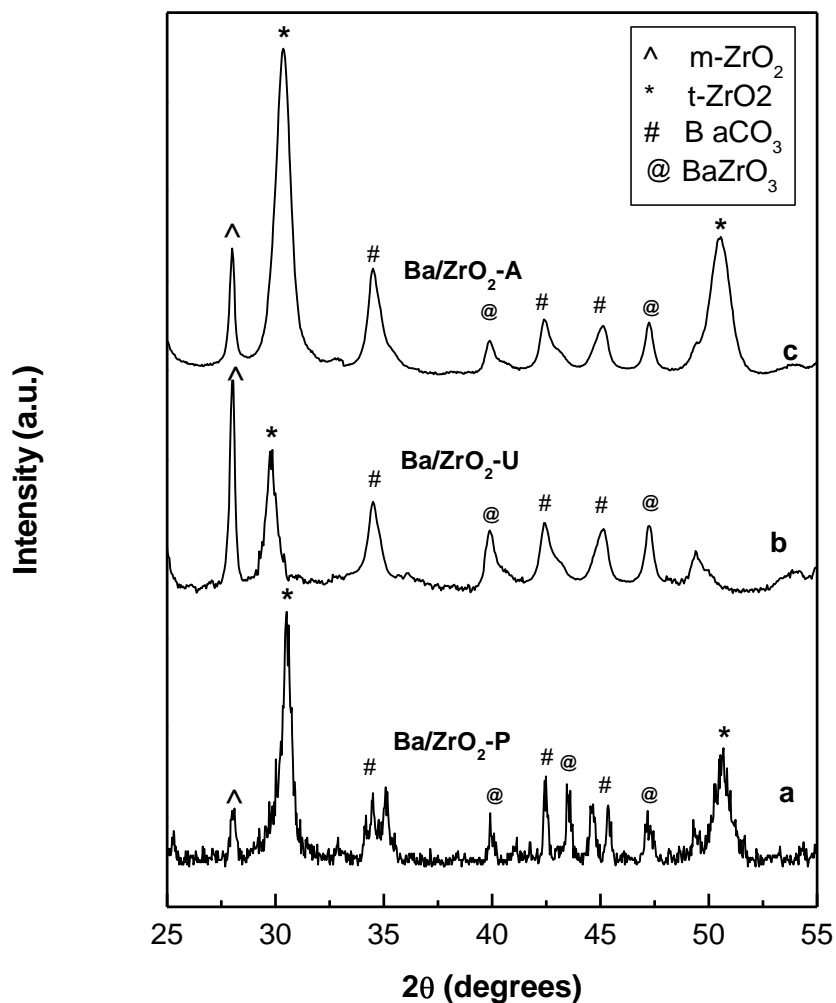


Figure 3.4 XRD patterns of (a) Ba/ZrO₂-P, (b) Ba/ZrO₂-U and (c) Ba/ZrO₂-A.

The percentage tetragonal phase present in the Ba/ZrO₂ samples calculated using equation (1) is presented in table 1. The presence of barium marginally promotes the formation of the monoclinic form of zirconia. Nevertheless, the Ba/ZrO₂ samples contain predominantly the tetragonal phase of zirconia.

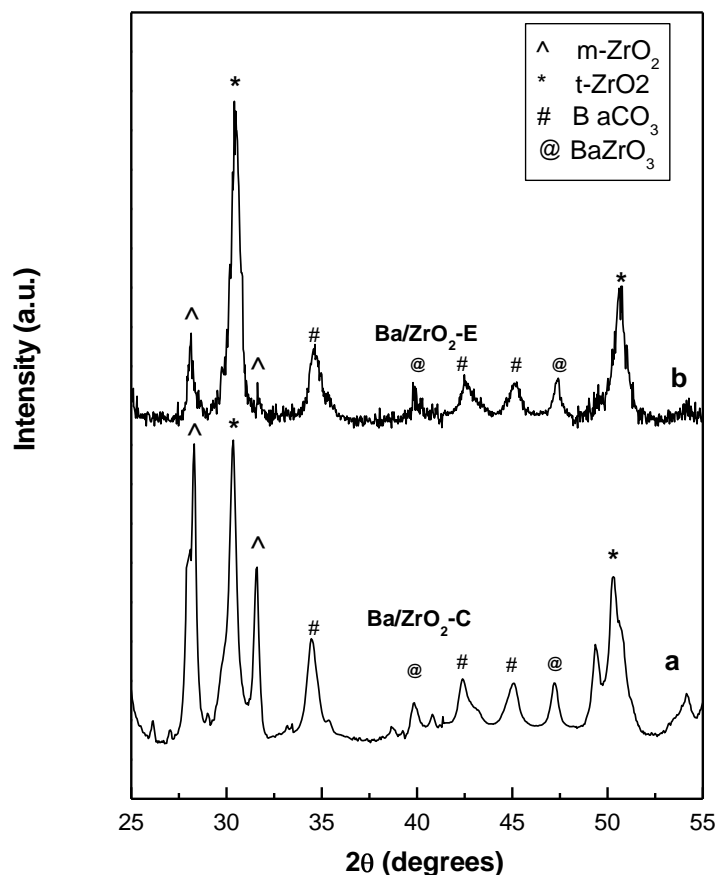


Figure 3.5 XRD patterns of (a) Ba/ZrO₂-C and (b) Ba/ZrO₂-E.

The crystallite size of the Ba/ZrO₂ sample was calculated from the Fourier line profile analysis of the broadened XRD peaks of the Ba/ZrO₂ samples. The representative pV vs L plot obtained from the Fourier analysis is presented in figure 3.6. The presence of particle varying in size and distribution is clearly evident from the plot and is strongly related to the method of preparation. The Ba/ZrO₂-A exhibit smaller particle size compared to other samples (Table 1). The particle

size trend observed for the Ba/ZrO₂ samples is similar to the pure ZrO₂ samples prepared using different preparative method.

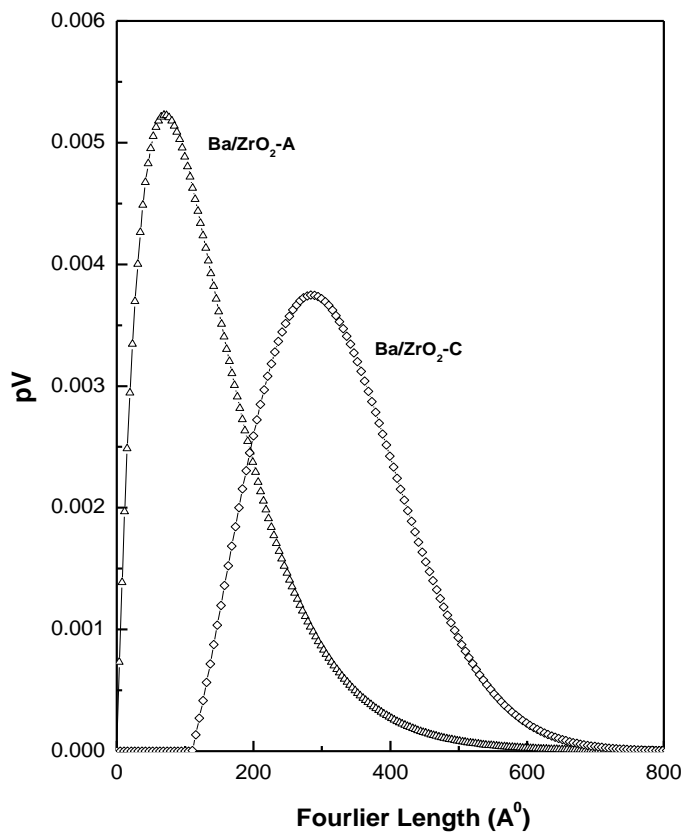


Figure 3.6 Fourier line profile analysis of Ba/ZrO₂-A and Ba/ZrO₂-C material.

3.2 IR study

The IR spectra of all zirconia samples prepared by different methods are presented in Figure 3.7.

In the stretching vibration region all the zirconia materials shows a prominent IR band in the range of 3400-3500 cm⁻¹.

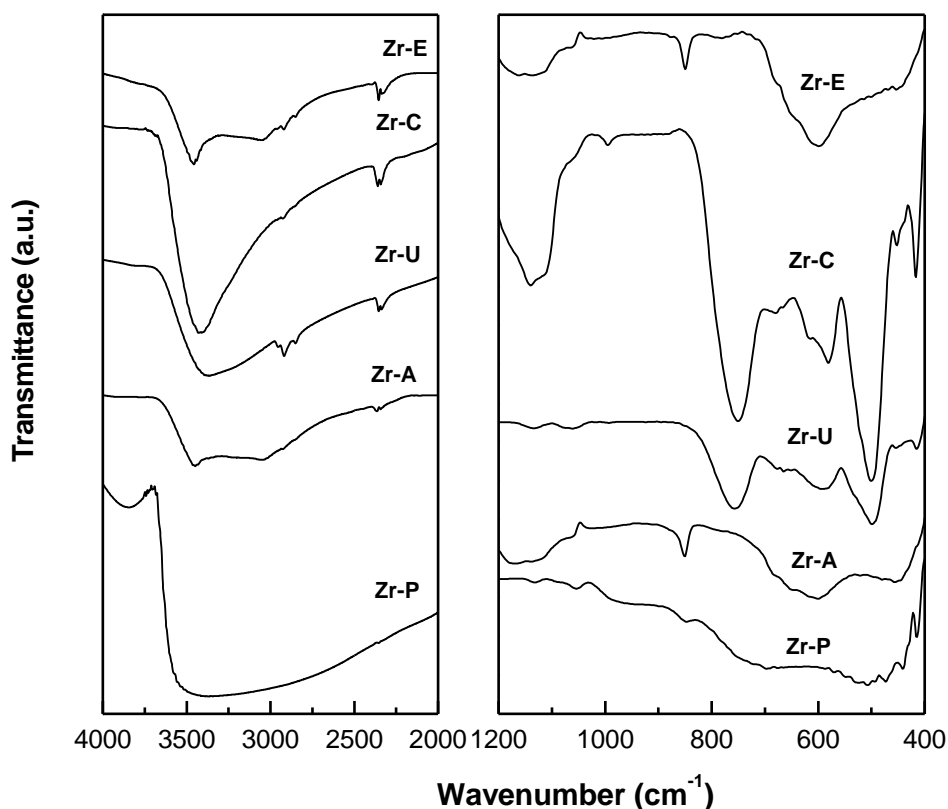
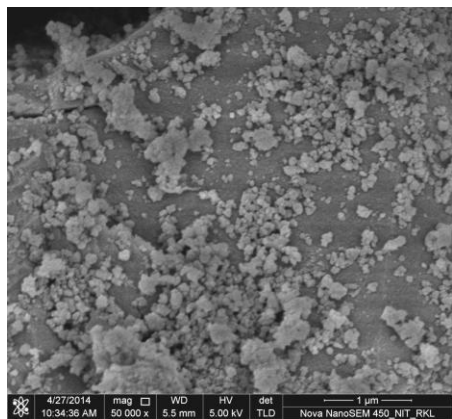


Figure 3.7 FTIR spectra of different zirconia samples.

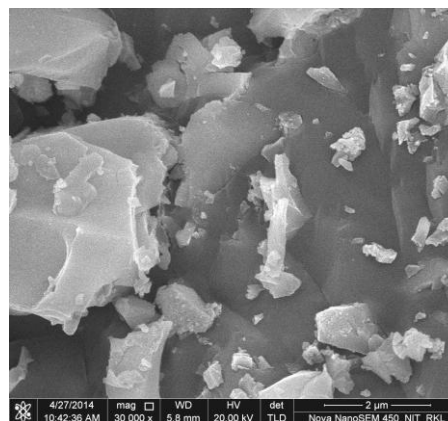
This band can be assigned to the O-H stretching vibration of adsorbed water as well as structural –OH group present on zirconia surface. In the bending mode region, the IR spectra of zirconia samples essentially show the various stretching frequencies at 445 cm^{-1} and 410 cm^{-1} (doublet), 500 cm^{-1} , 572 cm^{-1} , 740 cm^{-1} , 1104 cm^{-1} and 1187 cm^{-1} . The features particularly at 740 cm^{-1} and 500 cm^{-1} , due to Zr-O₂-Zr asymmetric and Zr-O stretching modes respectively, confirm the formation of ZrO₂ phases.

3.3 SEM study

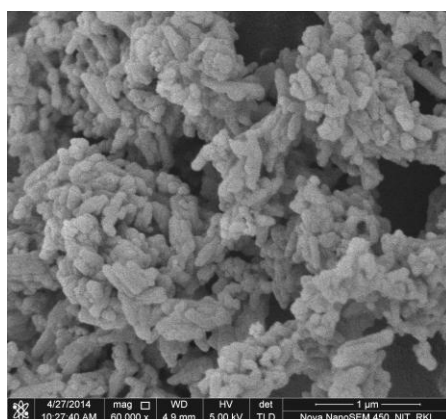
The field emission scanning electron micrograph of different Ba/ZrO₂ samples are presented in figure 3.8. The particles are of agglomerated and are of irregular shape and size.



(a)



(b)



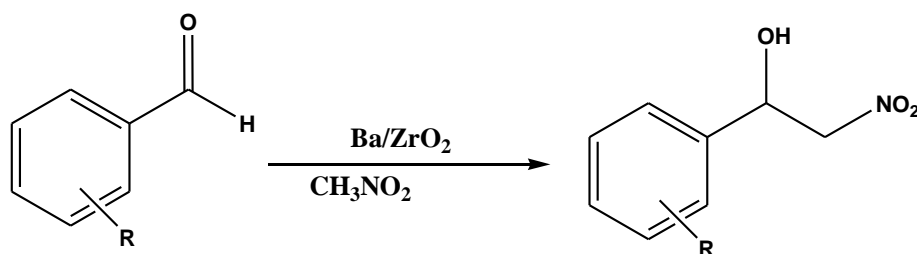
(c)

Figure 3.8 Field Emission scanning electron micrograph of (a) Ba/ZrO₂-U, (b) Ba/ZrO₂-P and (c) Ba/ZrO₂-E samples.

In case of the Ba/ZrO₂ samples prepared by urea hydrolysis, small particle growth is seen on the surface which is due to the formation of BaCO₃ and BaZrO₃ phases. The Ba/ZrO₂-E sample shows uniform particle morphology with rod shaped particles.

3.5 Catalytic studies

The Henry (nitroaldol condensation) reaction is one of the most significant C–C bond formation reactions which involve the synthesis of β -nitro alcohol by condensation of aryl aldehydes and nitroalkanes [13]. Since many natural products contains nitrogen atom, the Henry reaction provides a basis for development of such molecules. The β -nitro alcohol synthesized by the Henry reaction route is used as an intermediate for the synthesis of β -amino alcohol, amino sugar, ketones, pyrroles, porphyrins and pharmacologically potent compounds including fungicides, insecticides, antibiotics, natural products, and antitumor agents [14,15]. The various homogeneous and heterogeneous catalytic systems studied for this reaction include amine-MCM-41 hybrids, I_2/K_2CO_3 , silica-supported amine catalysts, and CsF/[bmim][BF₄] ionic liquids [13-15]. Most of the catalysts reported so far are either homogeneous catalysts or supported reagents which suffer from drawbacks such as leaching and recyclability. In this work, we have developed a methodology for the synthesis of nitro aldol products using Ba/ZrO₂ materials as catalyst (scheme 1).



Scheme 1. Synthesis of β -nitro alcohol catalyzed by Ba/ZrO₂ samples.

Initially, the condensation of p-nitro benzaldehyde with nitromethane in ethanol at 50°C was taken as a model reaction. The Ba/ZrO₂ samples were studied for their catalytic activity under the specified reaction conditions. Table 3.2 gives the catalytic activity of the Ba/ZrO₂ samples.

Among all barium containing samples the Ba/ZrO₂-U material gives higher yield of the product at short reaction time.

Table 3.2. Catalytic activity of different Ba/ZrO₂ materials for synthesis of β -nitro alcohol.

Sl No	Catalyst	Time (h)	Yield (%)
1	Ba/ZrO ₂ -A	10	65.1
2	Ba/ZrO ₂ -P	08	72.8
3	Ba/ZrO ₂ -C	10	58.2
4	Ba/ZrO ₂ -U	06	83.6
5	Ba/ZrO ₂ -E	06	78.4

The effect of temperature was studied for all the samples by varying the temperature between 30°C and 60°C (Figure 3.9).

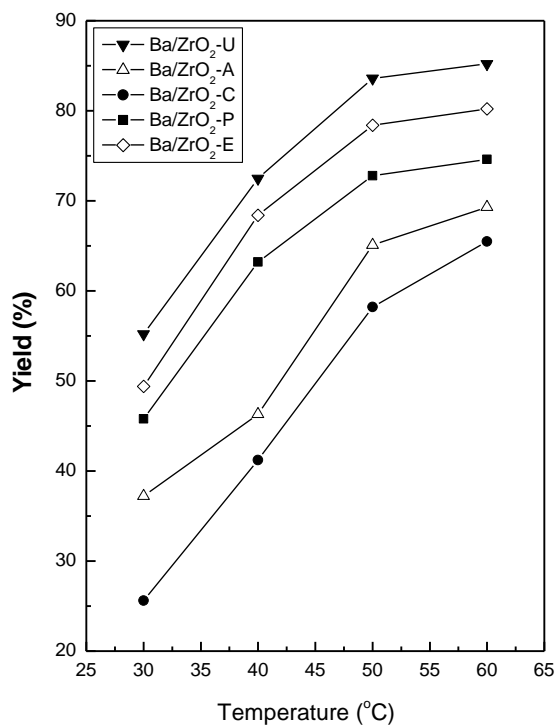


Figure 3.9 Effect of temperature on the catalytic activity of different Ba/ZrO₂ samples.

With increase in temperature the yield of the β -nitro alcohol was found to increase. However, there is marginal increase in yield beyond 50°C. Hence 50°C was chosen as reaction temperature for further study. After optimizing the temperature, the applicability of the protocol was further studied by using different substituted aldehydes in the optimized protocol. Table 3.3 shows the catalytic activity of Ba/ZrO₂-U catalyst for different substituted aromatic aldehydes. All the substituted aldehydes reacted efficiently in the optimized protocol to give moderate to good yield of the products.

Table 3.3 Catalytic activity of Ba/ZrO₂-U material for the synthesis of different β -nitro alcohols.

Sl No	R	Yield
1	H	72.6
2	4-NO ₂	83.6
3	2-NO ₂	81.2
4	4-Cl	75.8
5	2-Cl	77.2
6	4-OH	69.4
7	4-OMe	74.2

CHAPTER 4

CONCLUSION

In this work we have studied the preparation, characterization and catalytic application of barium modified zirconia particles for base catalyzed synthesis of β -nitro alcohols. The barium modified zirconia particles were synthesized by surface exchange reaction of zirconia with barium salt precursor. In order to study the effect of functionality and particle size of the zirconia particles on barium retention, zirconia samples were synthesized using five different methods. The zirconia samples contain both monoclinic and tetragonal phases. The relative content of the two phases depends strongly on the preparative procedure used. Highest tetragonal percentage was observed for the zirconia materials synthesized using amorphous citrate precursor route. The crystallite size of the synthesized zirconia was calculated using Fourier analysis of the broadened XRD profile of the zirconia samples. The urea hydrolysis method and the amorphous citrate methods are particularly effective for preparation of small nanosize zirconia particles. The XRD study of the Ba modified zirconia revealed the presence of barium zirconate and barium carbonate crystallographic phases along with the monoclinic and tetragonal form of zirconia. The IR spectra indicated the presence of various symmetric and asymmetric stretching characteristics to the zirconia samples. Growth of small particles over the surface of zirconia was observed in the barium modified sample from FESEM study. The barium modified zirconia particles were used as efficient base catalysts for synthesis of β -nitro alcohol by condensation of aryl aldehydes with nitromethane. The barium modified zirconia material was found to be active for the synthesis yielding a variety of β -nitro alcohol with good yield and purity. This work demonstrates the possibility of generating intrinsic basicity in the zirconia lattice by modification of its surface with barium ions. The materials developed in this work can be further utilized as catalyst for various base catalyzed reactions.

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