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Study of the influence of different synthesis methods and precipitating agents in generation of nanoparticles of zirconium oxide

Estudo da influência de diferentes métodos de síntese e agentes precipitantes na geração de nanopartículas de óxido de zircônio

DOI:10.34117/bjdv5n6-131

Recebimento dos originais: 30/04/2019
Aceitação para publicação: 02/05/2019

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ABSTRACT

Zirconia was synthesized and characterized by two different methods: homogeneous precipitation and polymeric precursors. For each method were assessed the conditions of synthesis for the generation of nanoparticles. In homogeneous precipitation method the generation of solid was studied in terms of precipitating agent (ammonium carbonate and/or urea) and calcination temperature of 450°C and 600ºC. In the polymeric precursor method, was studied the action of the esterificant agent (ethylene glycol and glycerol) and calcination temperature of 450°C and 600ºC. The materials were characterized by techniques of XRD, TG/DTA, FTIR, N_2-adsorption and TEM. An experimental design was performed using the

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Lorentz role representing the region of correlation for verification of effect of experimental conditions in the preparation of nanocrystals. Results show that variations in the synthesis results evaluated by each method do not significantly alter the generation of nanoparticles in the oxide, once both methods were promising for the generation of zirconium oxide nanoparticled in the range 6.1 to 15.9 nm. In general, among the methods employed can be noticed that the Pechini method using glycerol as an esterificant agent suites as a promising route for generation of nanoparticled zirconium oxide with good specific surface area and stabilizing the tetragonal phase.

Keywords: Synthesis of zirconia, homogeneous precipitation, polymeric precursors, Pechini method, nanoparticles.

RESUMO

A zircônia foi sintetizada e caracterizada por dois métodos distintos: precipitação homogênea e precursores poliméricos. Para cada método foram avaliadas as condições de síntese para a geração de nanopartículas. No método de precipitação homogênea, a geração de sólidos foi estudada em termos dos agentes precipitantes (carbonato de amônio e / ou ureia) e temperatura de calcinação de 450 ° C e 600 °C. No método dos precursores poliméricos, estudou-se a ação do agente esterificante (etilenoglicol e glicerol) e a temperatura de calcinação de 450 ° C e 600 ° C. Os materiais foram caracterizados por técnicas de DRX, TG / DTA, FTIR, adsorção de N_2 e TEM. Um planejamento experimental foi realizado utilizando a função de Lorentz para representar a região de correlação e verificação do efeito de condições experimentais na preparação de nanocristais. Os resultados mostram que variações nos resultados das sínteses avaliadas por cada método não alteram significativamente a geração de nanopartículas no óxido, uma vez que ambos os métodos foram promissores para a geração de óxido de zircônio nanoparticulado na faixa de 6,1 a 15,9 nm. Em geral, dentre os métodos empregados pode-se observar que o método Pechini utilizando o glicerol como agente esterificante se apresenta como uma rota promissora para geração de óxido de zircônio nanoparticulado com boa área superficial específica e estabilização da fase tetragonal.

Palavra-chave: Síntese da zircônia, precipitação homôgenea, precussores poliméricos, método Pechini, nanopartículas**.**

1 INTRODUCTION

Due to its physical and chemical properties, the applications of zirconia are promising and the material has been employed in many industrially important reactions such as solid electrolytes in solid oxide fuel cells and sensors, catalyst/catalyst support, optical films, protective coating, membranes and dispersed phase in composite materials, hydroprocessing, oxidation of alcohols and synthesis of methanol and higher alcohols[i]. Zirconia, is a very interesting material because of its thermal stability, its mechanical properties, and its basic, acidic, reducing, and oxidizing surface properties[ii]. These properties depend on the microstructure and the crystalline phases, which are a function of the primary particle size

distribution, the degree of agglomeration, and the removal of defects during processing[iii].Chemically, zirconia is an amphoteric support similar to alumina with oxidizing as well as reducing capabilities[ii]. However, compared to these supports, the surface area of zirconia is usually rather low, in the order 20-50 m^2g^{-1}.

The problem of the low surface area in zirconia could be addressed through the use of alternative preparation methods. Different methods to prepare high-surface-area zirconium oxide and ultrafine particles have been reported in the literature and many authors have recently focused toward alternative preparation techniques such as: sol–gel methods[iv], homogeneous precipitation[v], hydrothermal processing[vi], spray pyrolysis[vii], chemical vapor deposition[viii], combustion synthesis[ix] and co-precipitation method[x] [xi]. Chuah et al found an easy route to improve the surface area of zirconia by digesting the precursor, hydrous zirconia, prior to calcinations and the resulting zirconia has a surface of around 250 m^2g^{-1} depending on the conditions used[xii]. Virgens et al observed that the specific surface area and the porosity of zirconia are affected by preparations variables and the solid with high specific area (112 m^2g^{-1}) was produced by using sol-gel method by aging in mother liquor, rinsing with ammonium hydroxide solution and centrifugation[xiii].

In order to improve the properties of zirconium oxide, new methods of synthesis were studied and developed, and already well known methods were optimized. This study led to increase the knowledge about the mechanisms involved in the synthesis of zirconium oxide. Among these mechanisms, generating nanoparticles stands out as a major technological advance in recent years to zirconium oxide studies [xiv]. It has been shown that tetragonal ZrO_2 can be stabilized with grain sizes smaller than the critical value of 10-40nm[xv]. The decreasing of generated particles size increases surface/volume ratio causing a significant elevation in specific surface area of the resulting material. The generation of nanoparticle oxides, in particular of zirconium, is not an easy process. Many parameters influence the particles size reduction such as agitation speed, pH, reagents concentration, reagents addition speed, synthesis and calcination temperature and others[xvi] . The synthesis of zirconium oxide by a reproducible method is a challenge due to the difficulty on controlling these many parameters. The homogenous precipitation and Pechini method present themselves as alternatives for generating nanoparticles of zirconium oxide in oppose of sol-gel method which is traditionally used. The improvement of synthesis conditions for these methods and properties of materials have been showing great developments in the field of materials, however the generation of nanomaterials with dimensions below 10nm still is not verified

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with reproducibility[xvii]. The comparison of different methods allows the assessment of the most appropriate ones, not only in terms of material properties improvement, but also the practicality of the synthesis process for operator, economic viability and labor risks are among other important variables. The present study aims to evaluate the achievement of the zirconium oxide nanostructure with dimensions around 20nm by both Pechini and homogeneous precipitation methods, and optimization synthesis conditions to improve the material properties.

2 EXPERIMENTAL

2.1 SAMPLE PREPARATION

Pechini method (ZP)

The samples were prepared by adding simultaneous the following reagents: zirconium(IV) oxychloride octahydrate P.A, $ZrOCl_2.8H_2O$, Citric Acid, Glycerin and Ethylene Glycol. The reagents zirconium oxide chloride, citric acid and a polyhydroxy alcohol (ethylene glycol or Glycerin) were mixed in the ratio (1:5:15)xviii, into a beaker with deionized water. During the reagents addition the system was kept under stirring in oil bath at 120°C for 2h to esterification. The material was dried at 190ºC for 24h and calcined at air with temperature increase rate of 4°C/min, followed by 2 hours heating in temperatures of 450°C or 600°C. The solid thus obtained was ground and sieved in 100 mesh. The samples were named ZP3A, ZP3B, ZP4A and ZP4B, where the samples using ethylene glycol as agent precipitant were nominated by 3, the whereas with glycerol by 4. The letters A and B indicate the calcination temperature of 450°C and 600°C respectively [xix].

Homogeneous precipitation (ZH)

In the first step, 5.0000g samples of $ZrOCl_2.8H2O$ were dissolved in an aqueous hydrochloric acid solution (0.5mol L^{-1}) were added to a beaker and mixed with precipitating agent (urea or ammonium carbonate), molar ratio (1:3). The resulting solution was heated to 90°C on an electric plate to decompose the precipitating agent leading to the formation of the hydrous oxide [xx]. The final pH was adjusted to 9 using an ammonium hydroxide solution (1%). The white precipitate was stirred for 24h and then centrifuged (3000 rpm, 5 min), and then washed repeatedly with deionized water for the removal of chloride traces. These processes were repeated several times until no chloride ions were detected in the supernatant anymore. In the final step the precipitate was dried at 120ºC for 24h and calcined at air with temperature increase rate of 4°C/min, followed by 2 hours heating at temperatures 450°C

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and 600°C respectively[xix]. The solid thus obtained was ground and sieved in 100 mesh. Four samples were synthesized: ZH5A, ZH5B, ZH6A and ZH6B, where the samples using urea as agent precipitant were nominated by 5 and with ammonium carbonate by 6. The letters A and B indicate the calcination temperature of 450°C and 600°C respectively.

2.2 CHARACTERIZATION OF CERAMIC POWDERS

The eight samples synthesized were characterized by x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Transmission electron microscopy (TEM), Nitrogen adsorption and specific surface area measurements. The XRD powder patterns of the solids were obtained using about 300mg of powder on a diffractometer XRD-6000, Schimadzu using Cu Kα (λ = 0.15420 nm) radiation and nickel filter, in a 2θ range between 10° and 80° with a scanning speed of 2°/min. FTIR analyses were conducted in a Perkin Elmer equipment, model Spectrum One, in the range of 4000~450cm^{-1}. 50mg of the samples were prepared as potassium bromide discs, in a 1:10 proportion. Nitrogen adsorption and the specific surface area measurements were carried out by the BET method in an automatic Analyzer equipment of physical adsorption, Micrometrics, model ASAP 2010, where approximately 0,5g of the samples were used packed in quartz cell. The images of TEM were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. TEM specimens were prepared by ultrasonically dispersing the powder samples in ethanol (Merck, Pro Analysis) and then applying drops of this suspension to a holey carbon film supported on a copper grid.

3 RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION (XRD)

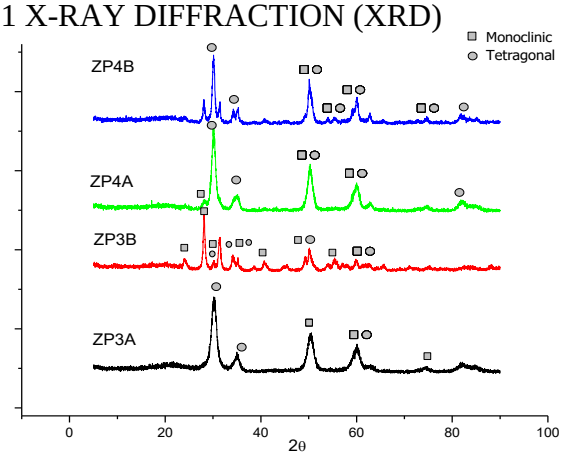

Figure 01: X-ray diffraction of zirconium oxide synthesized by Pechini method

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For all samples synthesized by polymeric precursor's method, the presence of tetragonal and monoclinic phases for zirconium oxide is shown on Figure 01. In samples synthesized with a higher calcination temperature, ZP3A and ZP4B, is observed in the range of 2θ (38 to 48) the formation of small intensity peaks not observed in samples synthesized at 450°C, indicating reduction in the material crystallinity. Through the data patterns of diffraction ASTM, samples synthesized with ethylene glycol, ZP3A and ZP3B, show tetragonal and monoclinic phases, a greater tendency to the formation of monoclinic phase with higher temperature indicating that ethylene glycol favors the stabilization of this last phase. Samples with glycerol mostly formed tetragonal phase, with presence of both phases tetragonal and monoclinic. This indicates that there was a modification of phases obtained from the use of glycerol in relation to the use of ethylene glycol.

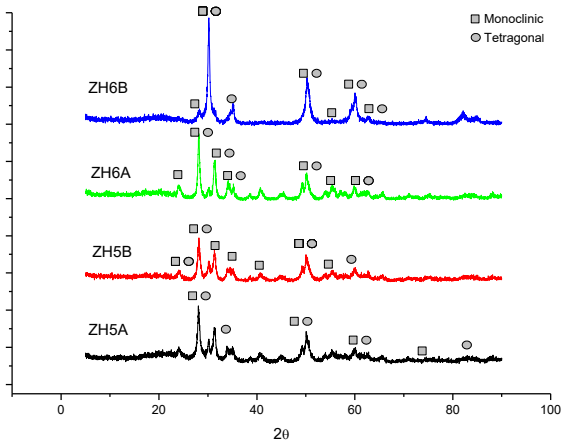

Figure 02: X-ray diffraction of zirconium oxide synthesized by homogeneous precipitation reaction.

For urea synthesis performed on samples ZH5A and ZH5B, Figure 02 indicates that elevation of temperature changed the predominant phase, metastable tetragonal, for monoclinic. The increase of calcination temperature from 450°C to 600°C generates a tendency for agglomeration of particles to stabilize thermodynamically, favoring monoclinic phase formation, which has a smaller superficial area than the tetragonal phase. It occurs due to particles agglomeration favored by the decrease in Gibbs energy. For ammonium carbonate, generated solid was polymorphic and mostly on monoclinic phase, independent of temperature used in calcination, but the increase of temperature caused an increase in the material crystallinity.

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3.2 PARTICLE SIZE BY XRD

An experimental plan was made to verify the influence of experimental conditions on formation of nanocrystals. The response factor used is the average size of the particle was calculated by Scherrer equation, from analyses of XRD[xxi]. The diffraction peak used for determining the width at half height was 2θ = 30, characteristic for all samples analyzed. The parameters W (peak width at half height) and 2θ were obtained on the ORIGIN software, with data of x-ray analysis in the region of the peak used. The Lorentz function was used to represent this correlation.

Correlation indexes provided by adjusting curves showed values above 0.9800 for the most of cases, indicating a good adjust and great reliability in the use of these parameters. Table 01 indicates to all samples: the main peak width at half height in degrees {W (2θ)}, in radians {W (rad)}, the diffraction angle 2θ used, the average size of the particle L (nm) and the range of sizes generated by different samples in each method. The calculation was performed by the Scherrer equation, excluding the third term for the micro deformity of the material. All samples analyzed, independent of the method employed, generated nanoparticled zirconium oxide in a narrow range between 6.1nm and 15.9nm.

Table 01: Value of the average size of the crystals from the width at half height of the peak (W)

Samples	W (2θ)	W (rad)	2θ	L (nm)	Range
ZP3A	1,348	0,0235	30,21	6,1	6,1 – 15,9 Δ = 9,8
ZP3B	0,518	0,0090	31,37	15,9	
ZP4A	0,963	0,0168	30,13	8,5	
ZP4B	0,579	0,0101	30,11	14,2	
ZH5A	1,34503	0,0235	30,21	6,1	6,1 – 14,7 Δ = 8,6
ZH5B	0,55847	0,0097	30,11	14,7	
ZH6A	0,96218	0,0168	30,13	8,6	
ZH6B	0,57483	0,01	30,11	14,3	

Comparing the average size of these samples one can observe that the samples generated with lower calcination temperature, without exception, have smaller sizes than samples calcined at 600ºC. In this specific case the elevation of temperature lead to the aggregation of smaller particles.

3.3 STATISTICAL ANALYSIS

A statistical tool was employed to compare data from different groups: ANOVA, available on Microsoft Excel software on Windows system. This tool performs a simple analysis of variance of the data from two or more groups of samples. The analysis tests the hypothesis that each sample is taken from the same underlying probability distribution against the alternative hypothesis that the probability distributions are not the same for all samples. This proves that the methods modifications were efficient for generating nanoparticles in values so close that can be considered the same probability distribution. In ANOVA tool, the factor value "F" defines this condition. If the calculated F value is lower than the critical F, then the different groups are under the same probability distribution. The analysis was carried out by separating the samples into two distinct groups as Table 02: Pechini (1) and homogeneous precipitation (2) synthesis.

Following the proposed treatment, the factor F was calculated and its value was lower than the critical F, concluding that the responses for the distinct groups were related to the same probability distribution and thus all methods were effective for generation of nanoparticled zirconium oxide in the same distribution range of average particles size. Analyzing the influence of each parameter of the synthesis to generate nanoparticles, the program SPSS statistic was employed in the construction of Pareto diagrams, which verifies the influence of each parameter investigated for the methods and the interactions between them.

Table 02: Results of ANOVA analysis for the four groups of samples.

SAMPLES	Pechini	Homogeneous Precipitation
Average size of particles (nm)	6,1	6,1
	15,9	14,7
	8,5	8,6
	14,2	14,3
SUMMARY		
Group	*Sum*	*Average* *Variance*
Pechini	44,7	11,175 21,46
Homogeneous Precipitation	43,7	10,925 18,11
ANOVA		
Source of variation	*F*	*P-value* *Critical F*
	0,130	0,941 3,490

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In the analysis of pareto diagrams for both methods of homogeneous precipitation and Pechini, the calcination temperature has greater effect on the increase of the average size of particles than all other variables. As already verified in the analysis of X-ray diffraction, the elevation of temperature probably causes the aggregation of smaller nuclei formed by metastable tetragonal phase, increasing the size of the particles and also inducing the formation of Ionic vacancies in the form of anions due to displacement of oxygen atoms in the Crystal structure[ix].

3.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

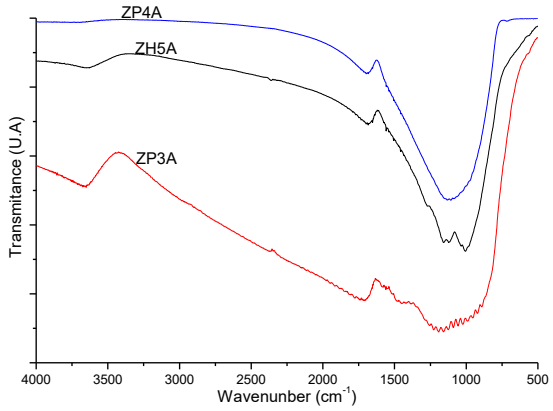

Figure 03: Infrared Spectroscopy for homogeneous Precipitation samples Z5A-H and Pechini Z4A-PC and Z3A-PC.

It is possible to verify on Figure 03 that all samples had bands around 3440cm^{-1} concerning [xxii] stretching vibrations of hydroxyl groups and residual water present in solids. There is an enlargement of this band due to the presence of only one hydroxyl group attached to the Zr^{4+} cation (3850cm^{-1}) or hydroxyl groups coordinated over more than one cation of Zr^{4+} (3740cm^{-1} and 3680cm^{-1}). The band near 1625cm^{-1} can be assigned to angular deformation of water molecules. The three absorption bands at 1340, 1220 and 992cm^{-1} along with other small bands located between 1450cm^{-1} and 900cm^{-1} are reported as traces of organic compounds in zirconium oxide in calcination temperature at 450°C generated by homogeneous precipitation and Pechini method. The bands below 1000cm^{-1} are assigned to connections Zr-O[xxiii] or the presence of chloride ions; however the Mohr test was negative after successive washes, indicating that the removal of the chloride ions was effective.

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3.5 TEXTURAL CHARACTERIZATION

In table 03 are the samples analyzed and the commercial zirconium oxide FZ0992, ZC code supplied by MEI Company, which was used as parameter. The results show that the zirconium oxide has heterogeneous textural characteristics, depending on the methods employed and its applied variables.

Samples synthesized by Pechini method showed results of textural characteristics apparently controversial once the samples synthesized with ethylene glycol had smaller average size than the synthesized with glycerol, but presents a smaller specific surface area and smaller pore volume. Observing the distribution of pores of both in Figure 4(a) and (b), one can assign this behavior to the irregular distribution of the sample Z3A-PC, which has large number of particles with diameter between 300Å and 900Å.

Table 03: Textural Properties of the samples selected for comparison between the methods and conditions of synthesis.

Code	SBET ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)	Pore Diameter(Å)	Average size of the crystal (Å)
ZP3A	40,8	0,08	81,9	61
ZP4A	64,5	0,11	57,3	85
ZH5A	78,8	0,08	44,7	61
ZC	100,0	0,20	38,0	-

This situation is not observed in the sample ZP4A, which has a monomodal distribution of pores in the range between 10 and 100th. Therefore, the synthesis with glycerol was more stable and homogeneous, favoring the textural characteristics of the solid. Compared to the commercial oxide, the samples synthesized by Pechini method presented smaller specific surface area and pore volume, and greater pore diameter.

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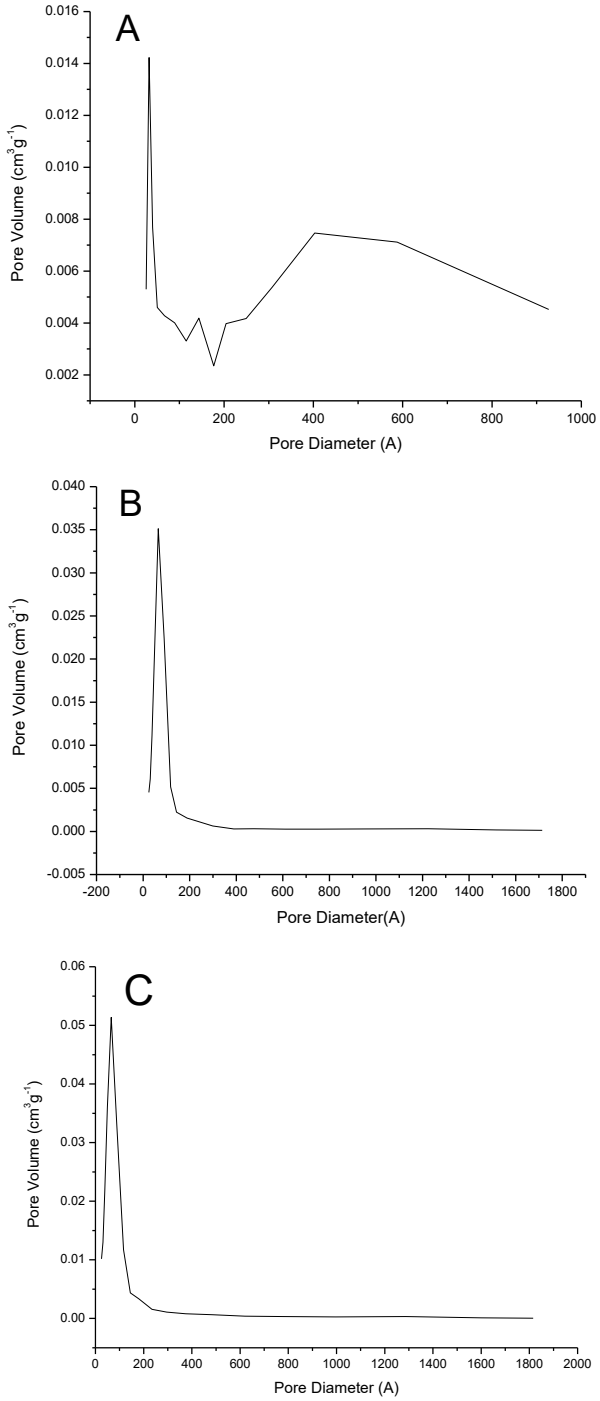

Figure 04: Distribution of pore volume for samples (A) Pechini with ethylene glycol, (B) Pechini with glycerol, (C) homogeneous precipitation with urea.

The phenomenon leads to decrease of surface material. This phenomenon has been successfully avoided through doping material with cations stabilizers[xxiv][xxv] which could improve significantly the textural properties of zirconium oxide prepared by Pechini method.

The synthesis by Pechini method occurs by decomposition of organic material by

pyrolysis and crystal phase formation by reaction of cations with oxygen ions of the polymer or from oxygen in the air. After a chemical reaction, the precipitation process occurs by nucleation and growth. As a very large number of particles will interact, the process of coalescence growth of particles can be well represented by the model called "Ostwald ripening"[xxvi]. The model considers that large particles have lower solubility than small particles, when they are in equilibrium with a particle saturated solution[xxi]. This way, the small particles must be dissolved, while the large particles must grow. In the case of ceramic powders obtained by Pechini method, the smaller particles have a much greater fraction of atoms at the surface than larger particles. The excess energy of the surface causes small particles disappear simultaneously the growth of large particles

For the sample synthesized by homogeneous precipitation the specific surface area and pore volume did not follow this tendency, although its average diameter is smaller than the others, Figure 4(A,B). Probably decreased specific surface area is related to this bimodal distribution on pores in Figure 4(C), in the range between 10~100Å and macropore above 600Å, which may have been caused by the sintering of small particles as a function of the large number of nuclei formed in this synthesis. The increasing of surface free energy causes a tendency to raise particles with expressive reduction of specific surface area.

Isotherms of adsorption/desorption of nitrogen were evaluated for samples of zirconium oxide. The isotherms are shown in Figure 05 and all are classified as type IV [xxvii][xxviii][xxix], characteristic of well-developed systems oxides (pores between 20 Å and 500 Å). For all samples the phenomenon of hysteresis, coming from the difference between the processes of adsorption and desorption of gas. This occurs because for mesopore and macro-pore solid, the evaporation process is different from the process of condensation. When condensation occurs inside the pores, where the forces of attraction are larger due to the proximity between the molecules, this can occur at pressures lower than in non-porous solids. However, the pore format difficult the evaporation, indicating its structure.

The ZP3A presents more discreet phenomenon of hysteresis among the samples, resembling a lot with an isotherm of type II. A rapid increase in the amount of gas adsorbed to low values of relative pressure is verified, which makes it slower to intermediate values of P/Po. Probably the first strong interactions of gas molecules with more active sites of solid cause this behavior. After filling these sites, the gas interacts with the lower energy sites[xxvii]. In the end of the curve occurs a rapid increase in the amount of gas adsorbed on

function of the relative pressure.

This is due to the beginning of the formation of multiple layers and subsequent condensation. In the sample ZP4A the phenomenon of hysteresis occurs with greater intensity, indicating greater dispersion of pore size. This is evidenced by the graph of distribution of pores in Figure 4b. For the sample synthesized by homogeneous precipitation method, ZH5A, the phenomenon occurs due to the presence of large amount of Macropores, verified by the graph in high concentration from 800Å.

Samples of Pechini from Figures 5(A) and (B) has hysteresis Type H3, characteristic by two branches of the isotherm, asymptotic over relative pressure on P/Po equal to unity. This behavior is associated with not hard particle aggregates shaped Board, resulting in pores on crack.

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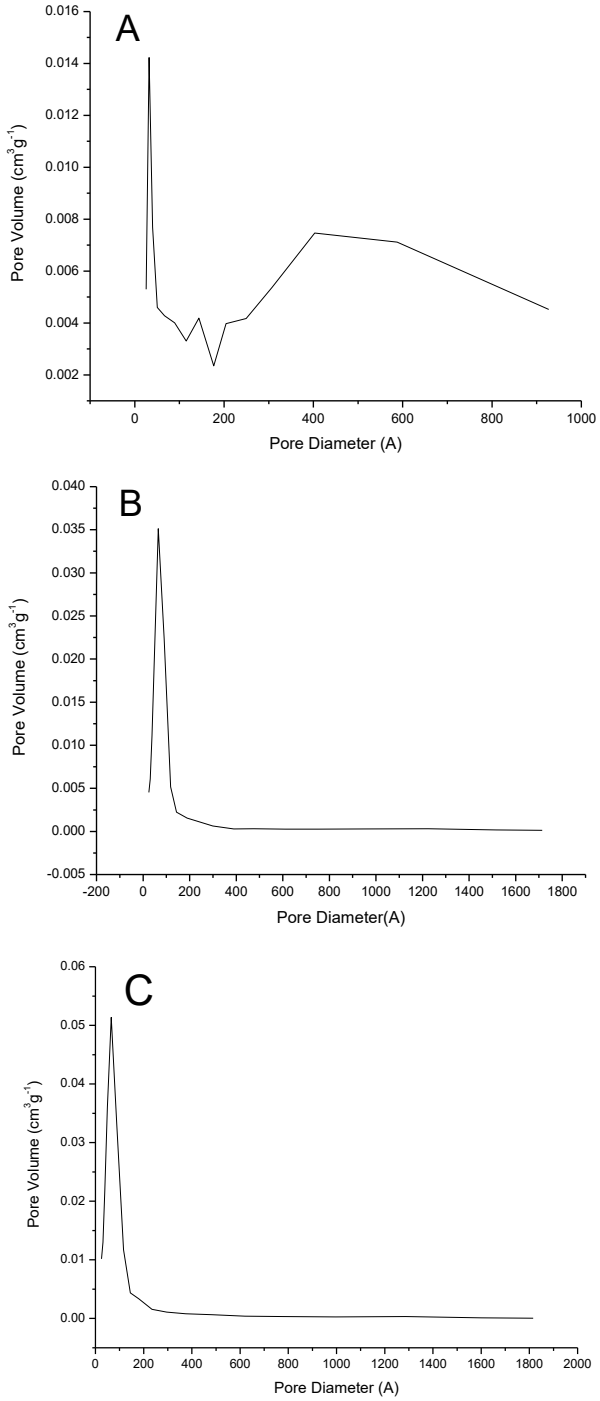

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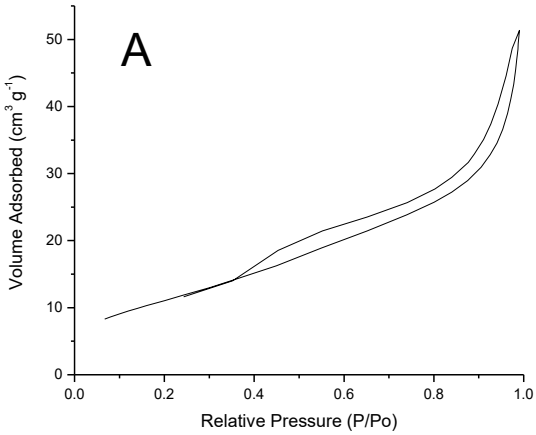

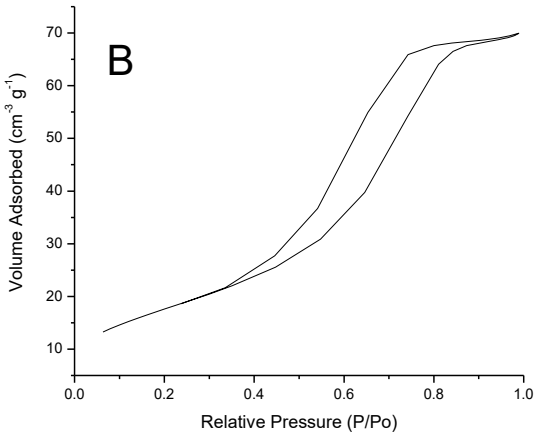

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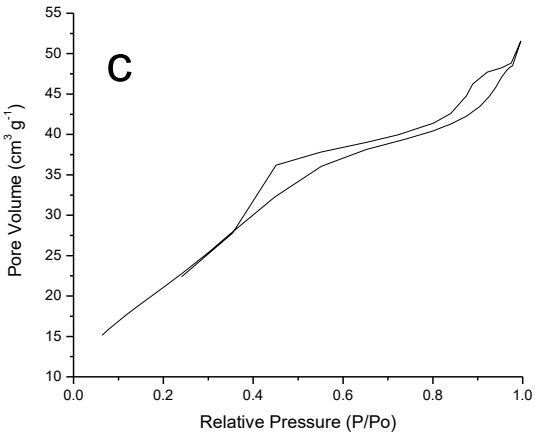

Figure 05 : Adsorption/desorption Isotherms for samples (A) Pechini with ethylene glycol, (B) Pechini with glycerol, (C) homogeneous precipitation with urea.

For homogeneous precipitation sample, shown in Figure 5(C), hysteresis H4 is evidenced by two branches of the isotherm almost horizontal and parallel over wide range of relative pressure variation. This type is also associated with narrow pores in cracks.

3.6 MICROSCOPIC ELECTRONIC TRANSMISSION

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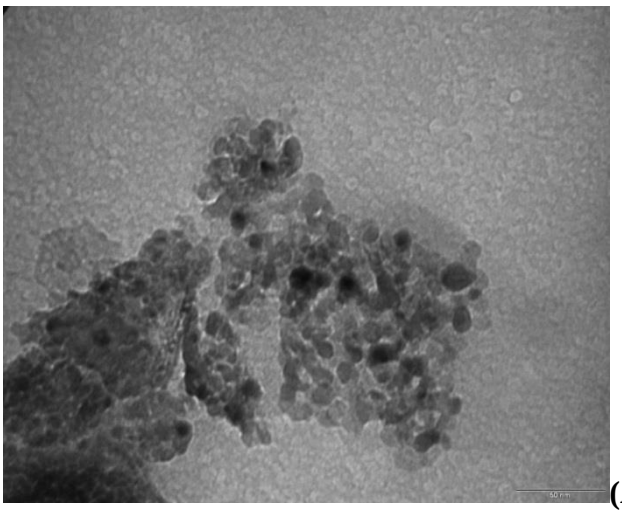
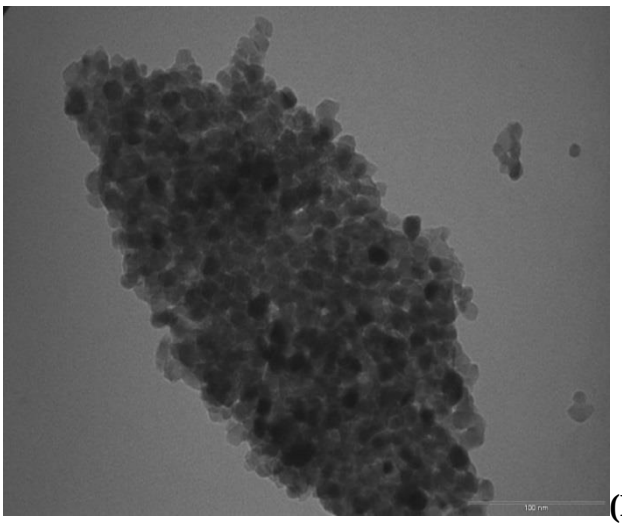
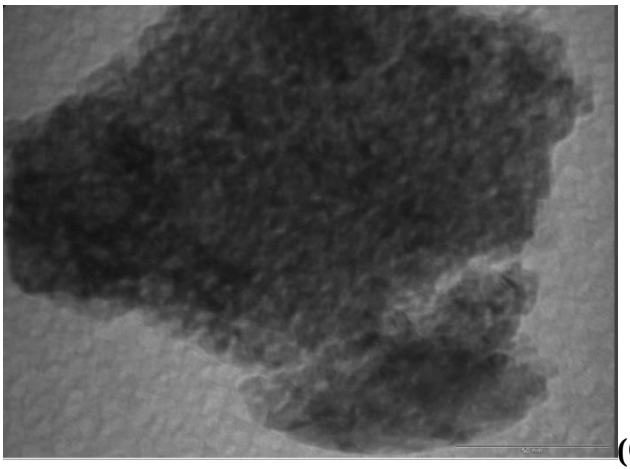


(A)



(B)



(C)

Figure 06: Micrograph of samples of the Pechini ZP3A (A), ZP4A(B) and homogenous precipitation respectively ZH5A(C).

TEM micrographs of some of the representative methods are shown in Figure 06. In the ZH5A samples, no clear particles can be observed and all are adhere to each other, forming hard agglomerates. The ZP4A sample consists of irregular spherical grains and the

grain sizes are in the range of 6~15nm. The ZP3A sample has the similar morphology, but its gain sizes are about 15~30nm, relatively larger compared with ZP4A. It is clear that the obtained ZrO_2 nanocrystals in the presence of glycerol are smaller than the obtained ZrO_2 in the presence of ethylene glycol as agent precipitant but these products are agglomerated. It may be noted that modification of the precipitating agent promotes a change in process of growth of crystallites. This observation is in agreement with the respective pore volumes shown in Table 3.

4 CONCLUSIONS

All modifications proposed on the synthesis of zirconium oxide by Pechini and homogenous precipitation method generated samples around 10~15nm, specially the sample synthesized by Pechini method with glycerol. This latter sample showed a homogeneous distribution and homogeneous average pore volume, becoming a promising method to obtain nanoparticles of zirconium oxide.

ACKNOWLEDGEMENTS

This present work has been supported Universidade do Estado da Bahia, UNEB, and Universiade Federal de Uberlândia, UFU, which provided financial and infra-structural resources.

Acknowledgements to the Grupo de Estudos em Cinética e Catálise, GECAT, from Universidade Federal da Bahia, UFBA, for providing support with equipment and analysis of x-ray diffraction.

Acknowledgements to the Doctor Denilson Rabelo and the Universidade Federal de Goiás, UFG, for providing support with the superficial area analysis.

And to Rita Alves da silva.

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