

Synthesis of Nanosilica Powders by Recovering an Effluent from Pure Zirconia Powder Production Process via Wet Chemical Processing

C. Yamagata, V. Ussui, J. D. Andrade, J. O. A. Paschoal

Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Centro de Ciência e Tecnologia de Materiais - Laboratório de Insumos, Caixa Postal 11049, Pinheiros, CEP 05422-970, São Paulo, Brasil
yamagata@ipen.br

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Abstract: A gel of coagulate silica was obtained from a mother zirconium oxychloride solution, produced by acid-washed zircon ($ZrO_2 \cdot SiO_4$) powder, processed by alkaline fusion reaction. When acid is added to this processed zircon, silica with primary particle is created. Radical dehydration condensation reaction is promoted at silano (Si-OH) on the surface primary particle by sufficient adding of acid and aging. As a result, (Si-O-Si) complex is formed and three dimensions structure is generated. This is so called silica gel. Physical properties are controlled by means of washing and drying process to produce micronized silica. In this paper, by recovering an effluent from pure zirconia powder production process, nanostructured silica powders with high specific surface area ($> 600 \text{ m}^2 \cdot \text{g}^{-1}$) were obtained. The infrared spectra of obtained silica gels calcined at 100, 200 and 800 °C were analyzed. Powders were characterized by BET method. QELS (Quasi Elastic Light Scattering) technique was used to determine particles size distribution. SEM and TEM were applied for morphological investigation of the particles.

Introduction

In recent years, the synthesis and characterization of nanosized structured particles has received substantial attention and has become an increasingly active field of science because of a large growing of nanomaterials applications in many fields [1, 2]. Silica nanoparticles offers a wide range of industrial applications [3] such as catalysis [4], pharmacy [5], pigments [3], sensors [6], bioceramics [7], electronic and thermal insulators, electronic and thin film substrates, etc. Nanoparticle silica is considered important mainly as catalytic support materials [4]. The performance and quality of these products are highly dependent on the size and size distribution of their raw materials particles. For example, high specific surface area is desirable for catalytic support because high surface area provides more active sites for gas-solid interactions. On the other hand, special attention must be given to the morphology of the powders, because it can improve or modify the mechanical, electrical or other properties of materials.

Commercial available SiO_2 nanopowders are produced by high-temperature aerosol process such as plasma and arc reactors or by flame hydrolysis/oxidation [8,9]. This investigation is concerned with recovering the contents (silica) of an effluent from pure zirconia powder production process and intends to get SiO_2 raw powder material for its application in many fields.

Experimental

A mother impure Zr-oxycloride solution was obtained from HCl dissolution of water washed zircon powder previous reacted with caustic soda by usual procedure [10]. A gel of coagulate silica was obtained from that mother zirconium oxycloride solution. The coagulated material is an effluent of pure zirconia powder production process. In Fig.1., flow sheet of pure zirconia powder production process is showed.

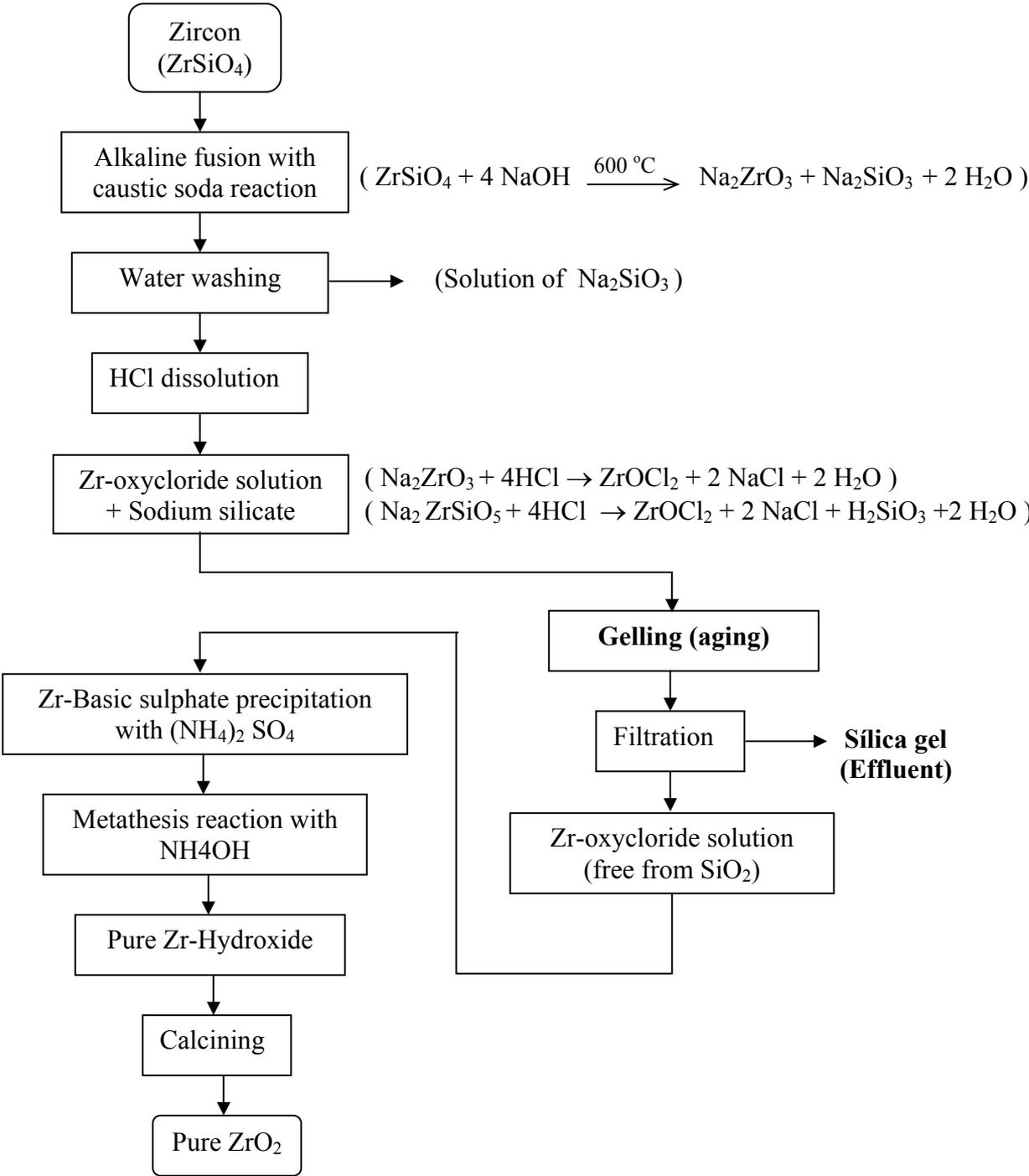


Fig. 1 - Flow sheet of pure zirconia powder production process.

In the process showed in Fig 1, when HCl is added to the processed zircon powder (HCl dissolution), silica with primary particle is created. Radical dehydration condensation reaction is promoted at silano (Si-OH) on the surface of primary particle by sufficient adding of acid and aging. In this work, 6M commercial HCl was used to carry out the acid dissolution of alkaline fusion processed zircon. After a day aging, gel of (Si-O-Si) complex was obtained in the Zr-oxycloride solution ($ZrOCl_2$). The resulted silica gel was separated from $ZrOCl_2$ by stirring the suspension followed by vacuum filtration. The gel was washed with distilled water until no chloride ion was detected by $AgNO_3$ test. The gel obtained from water washing was dispersed in butanol (analytical grade) and thermal treated at $107\text{ }^\circ\text{C}$ for 6 h. The volume of the suspension was maintained by refluxing the condensed liquid. Subsequently the suspension was filtered and the gel was dried in air for 12 h, at $80\text{ }^\circ\text{C}$ and calcined for 1 h at 100, 200 and $800\text{ }^\circ\text{C}$. The infrared spectra of calcined silica gels were analyzed. Powders were characterized by BET method. QELS (Quasi Elastic Light Scattering) technique was used to determine particles size distribution. SEM and TEM were applied for morphological investigation of the particles.

Results and Discussion

IR spectra of silica gel calcined at 100, 200 and $800\text{ }^\circ\text{C}$ are presented in Fig.2. The region where the infrared spectrum of water is found, i. e., bands between 3200 and 3550 cm^{-1} , shows that the sample calcined at $800\text{ }^\circ\text{C}$ has less adsorbed water than samples calcined at 100 or $200\text{ }^\circ\text{C}$. All samples show a Si-O-Si bending mode at 470 cm^{-1} and symmetric Si-O-Si stretching at 800 cm^{-1} and antisymmetric Si-O-Si siloxane stretching band centered between 1000 cm^{-1} and SiO_2 overtones at 1640 cm^{-1} . The C-H features at 1470 cm^{-1} and the C-H stretching at 2850 and 2930 cm^{-1} are observed in samples calcined at 100 and $200\text{ }^\circ\text{C}$. In the sample calcined at $800\text{ }^\circ\text{C}$ those bands are not verified; indicating that in this sample there are no organic residues of butanol, used in the process.

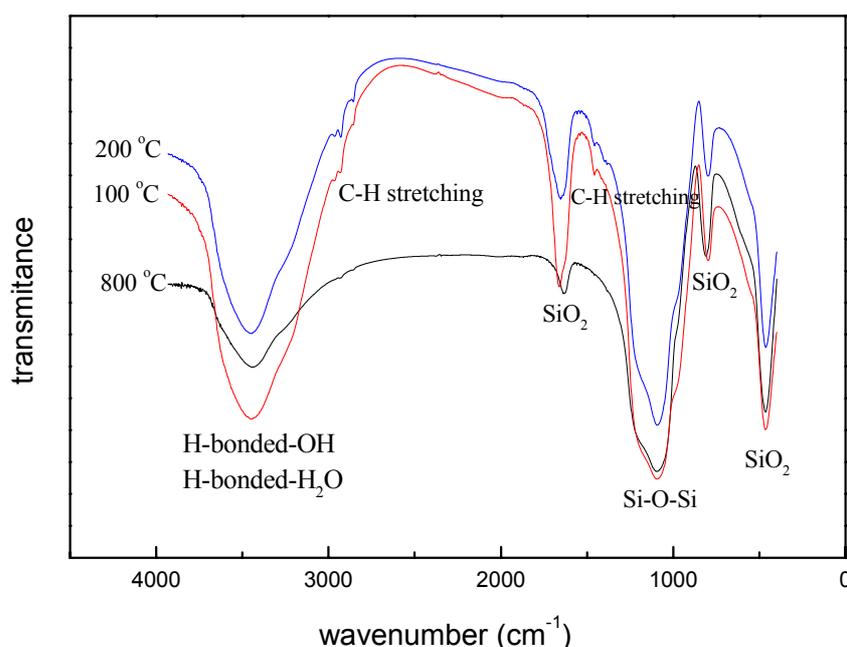


Fig.2 - IR spectra of obtained silica gel, calcined at 100, 200 and $800\text{ }^\circ\text{C}$.

Physical properties of final silica powder depend on washing, drying and thermal treatment process. The specific surface area measurements determined from nitrogen adsorption according to the BET (Brunauer, Emmet and Teller) method as a function of calcining temperature are given in Fig. 3. The specific surface area increases by increasing the temperature of thermal treatment up to 200 °C, where the highest value is observed. The specific surface area drops sharply at 800 °C. The lost of surface area at this temperature may be related to sintering of extremely small primary particles of the mass aggregates.

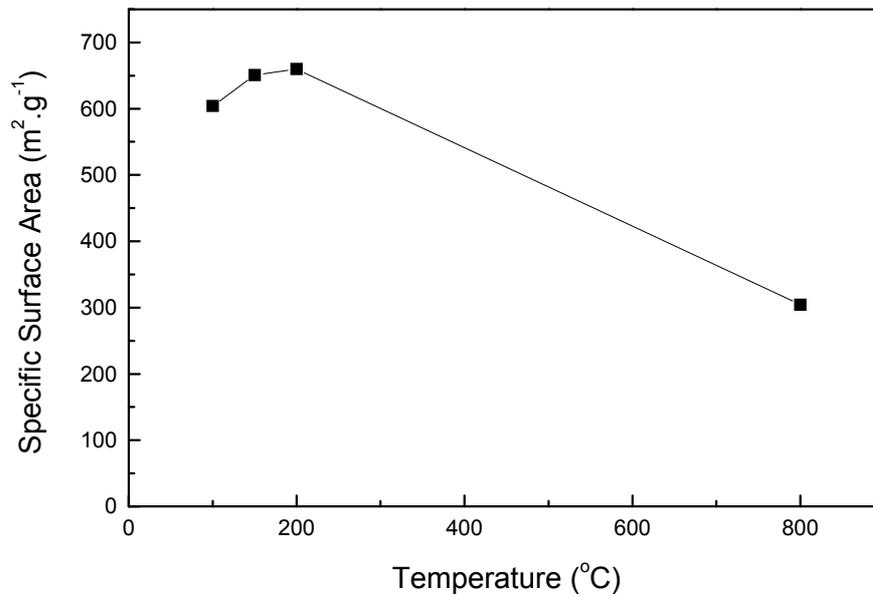


Fig. 3 - Specific surface area of silica powders as a function of calcining temperature.

Mean particle diameter size as a function of temperature of calcining, determined by QELS (Quasi Elastic Light Scattering) technique is presented in Tab.1. No significant variation of mean particle diameter size is observed from samples 1 to 2. A slight decrease is observed for sample 3 as it happened to specific surface area.

Tab. 1 - Mean particle diameter size, as a function of temperature of calcining.

Sample	Temperature of calcining (°C)	Mean particle diameter size (nm) (determined by QLS)
1	100	721,3
2	200	855,2
3	800	560,8

Eq. 1 was used to calculate the mean particle diameter size, for sample 3, where A_s is specific surface area; d_p , particle diameter; ρ_{app} , apparent density of the material (measured with helium). The value of calculated mean particle diameter size was 3.9 nm.

$$A_s = \frac{6}{d_p \rho_{app}} \quad (1)$$

This value is comparable to silica particle size produced by natural process in geothermal water, where the silicate ion $\text{H}_3\text{SiO}_4^{3-}$ or $\text{Si}(\text{OH})_3\text{O}^{3-}$ react with undissociated silicic monomers $\text{Si}(\text{OH})_4$ or other silicate ions to produce polymeric hydroxy silic chains which polymerise to form hydrous silica sol particles of about 4-8 nm [11].



Fig. 4 shows SEM images of the samples. It is observed agglomerates with similar morphology with submicron size particles in all samples.

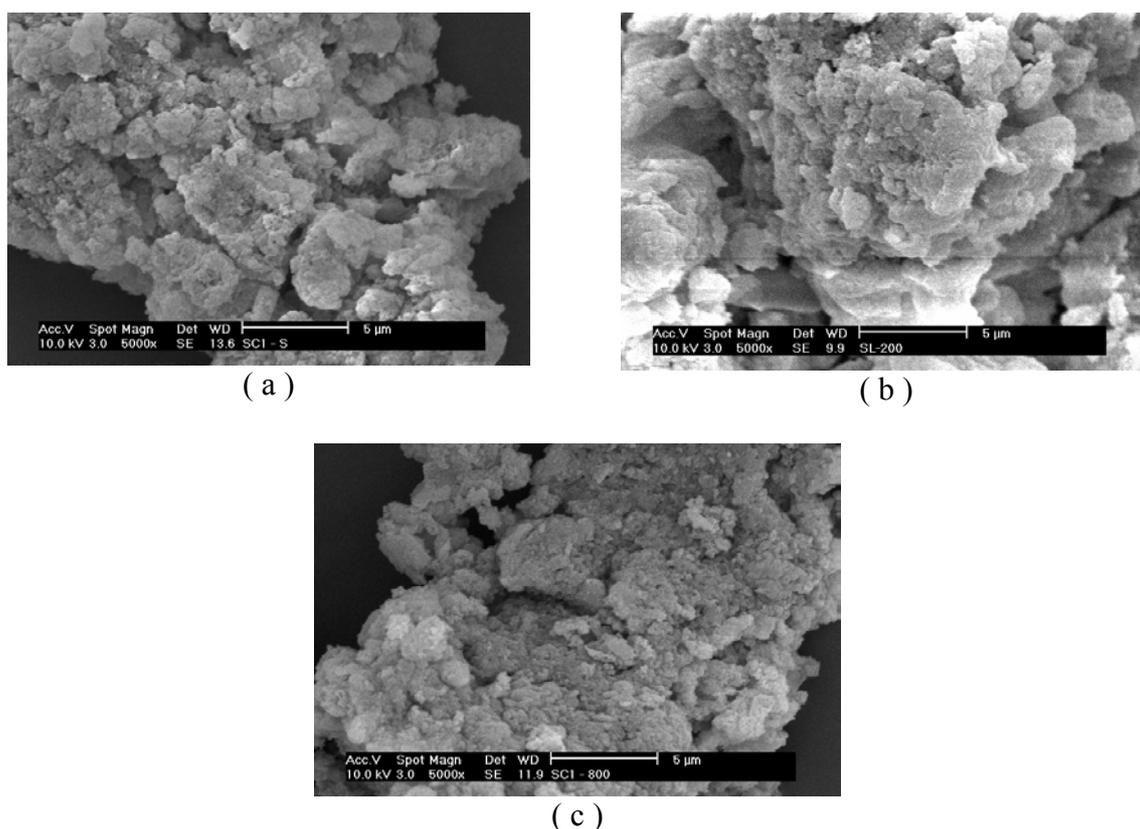


Fig.4 – SEM images of silica gel calcined at 100 °C (a), 200 °C (b) and 800 °C (c).

TEM image of sample 3, in Fig. 5, shows that the morphology of the agglomerates is spherical like and size about 60 nm, confirming that nano-structured silica was obtained.

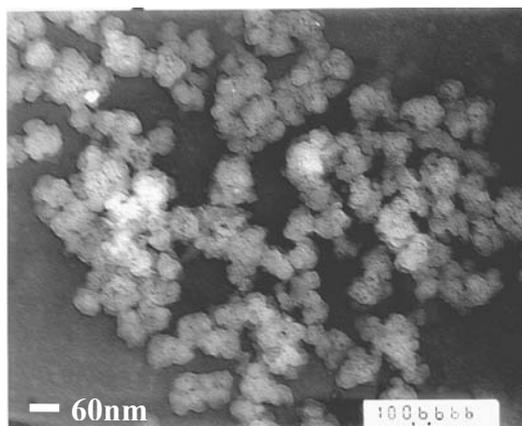


Fig. 5 – TEM image of obtained silica gel calcined at 800 °C.

Conclusions

Nanosized silica powders have been synthesized by recovering an effluent from pure zirconia powder production process. This inexpensive, low temperature process can be used to produce silica raw material to a variety of silica application, since powders with extremely high specific surface area ($> 600 \text{ m}^2 \cdot \text{g}^{-1}$) were obtained, presetting agglomerates of about 60 nm with primary particles comparable to those achieved by high temperature vaporization processes.

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