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Reflux synthesis and hydrothermal processing of ZrO2 nanopowders at low temperature

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Abstract – In this work, we report on the reflux synthesis at 90 ^oC and hydrothermal processing at 120 ^oC for obtention of zirconium oxide (ZrO_2) nanopowders under several conditions. These nanopowders were characterized by X-ray difraction (XRD), Fourier transform Raman (FT-Raman) spectroscopy, Adsorption-desorption N_2-isotherms and field-emission scanning electron microscopy (FE-SEM). XRD patters and Raman spectra indicated that ZrO_2 nanopowders present a monoclinic structure. In addition, the hydrothermal processing promoted an increase in crystallinity of ZrO_2 nanopowders. The morphology of ZrO_2 nanopowders was observed by FEG-SEM. Also, the FEG-SEM micrographs revealed that the presence of H_2O_2 in systems reduced the particle size, while the absence of promoted an increase in particle size.

Metallic oxides are a class of materials widely used as support in several applications [1]. among these oxides the zirconium oxide (ZrO_2) is very promissor to catalysis support. ZrO_2 can present three crystalline structure: tetragonal (t-ZrO_2), cubic (c-ZrO_2) and monoclinic (m-ZrO_2). Recently, ZrO_2 has received considerable attention as a catalyst for various reactions including hydrogenation of hydrocarbons, cracking, dehydrogenation and hydrodesulphurization. Therefore, in this paper, we report on the synthesis of ZrO_2 by reflux method and hydrothermal processing at 120 ^oC in diferent conditions. The aqueous solution of the precursors systems were prepared with appropriates quantities of reagents in distilled water, using four different method to obtain crystalline ZrO_2 nanopowders: *Method A* - Reflux at 90 ^oC for 96 h, $ZrOCl_2.8H_2O$ (Aldrich 99.9%) + H_2O_2 (Mallinckrodt, 10% in volume) in 50 mL of water. *Method B* - Hydrothermal processing at 120 ^oC for 72 h, $ZrOCl_2.8H_2O$ in water. *Method C* - Hydrothermal processing at 120 ^oC for 72 h, $ZrOCl_2$.8H2O + H_2O_2 in water. *Method D* - Hydrothermal processing at 120 ^oC for 72 h, $ZrOCl_2.8H_2O$ + H_2O_2 + NH_4OH (J. T. Baker, 30%) in water

In Fig. 1, it is possible to observe that with 72 h of reaction in hydrothermal system at 120 ^oC, the extent of the crystalline phase is formed in large quantities. Based on these results, the hydrothermal method was preferred to the reflux method for synthesizing nanozirconia (92 $m^2.g^{-1}$). It is possible to observe that the zirconia obtained in absence of hydrogen peroxide (H_2O_2) presents a well defined monoclinic structure and a large crystallite size (Fig. 1). In Fig. 2, it is possible to observe the peaks are very wide, due to presence of nanocrystalline phase and small crystallite size (192 $m^2.g^{-1}$). Crystallite size was estimated to be less than 10 nm even for the sample obtained after 96 h. Crystallinity was improved significantly at this time and the ZrO_2 with monoclinic structure is well defined. The crystallinity was confirmed by Raman.

In Fig. 3, can be observed a large number of spherelike ZrO_2 nanoparticles. However, in Fig. 4 it was observed the presence of rods-like ZrO_2 nanoparticles. This behavior of isotropic growth for ZrO_2 nanoparticles, can be attributed the use of 10% H_2O_2 as the agent oxidant, that acts in oxide surfaces and inhibit the anisotropic growth to self-assembled particles to formation of nanorods [2], can be observed in inset Fig. 4. The inset Fig. 3 its was verified that the sphere-like ZrO_2 nanoparticles present a spontaneous aggregation by interaction of Van der Walls during the coalescence process.

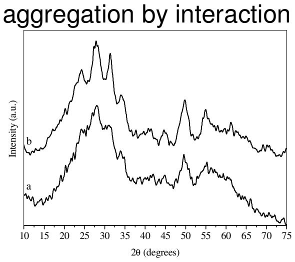

Figure 1: X-ray diffraction patterns of catalytic supports (ZrO_2) obtained from $ZrOCl_2.8H_2O$ in reflux. a) at 90 ^oC/2 days and b) 90 ^oC/5 days.

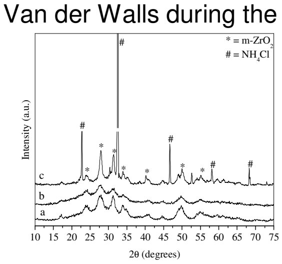

Figure 2: X-ray diffraction patterns of catalytic supports (ZrO_2) obtained from $ZrOCl_2.8H_2O$ in reflux. a) at 90 ^oC/2 days and b) 90 ^oC/5 days.

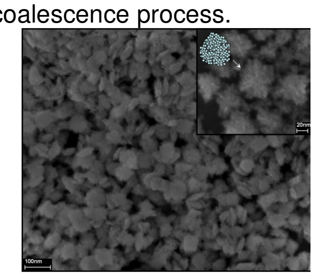

Figure 3: FE-SEM micrograph for th ZrO_2 nanopowders: (a) *Method A*

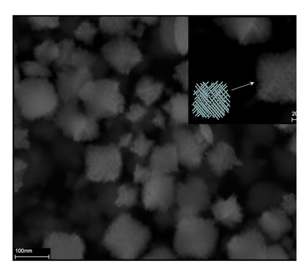

Figure 4: FE-SEM micrograph for the ZrO_2 nanopowders: (a) *Method A*

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