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Nanosilica synthesized by the Pechini method for potential application as a catalytic support

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Abstract

The purpose of this work was to synthesize and characterize silicon oxide (SiO_2) using TEOS as the source of silica to obtain a nano-ceramic material with potential for application as a catalytic support. The material, which was prepared by the Pechini method, was calcined at temperatures of 600, 700, 800 and 900 °C for 1 h. Nanosilica samples were characterized by X-ray diffraction (XRD), particle size distribution, surface area and pore size (BET/BJH), and scanning electron microscopy (SEM). The results indicate that amorphous material was formed at all the calcination temperatures applied, indicating the formation of nanosilica. Increasing the calcination temperature did not alter the amorphous structure of the nanosilica. The microstructures of the samples presented an irregular-shaped plate-like morphology and a wide particle size distribution. The BET analysis revealed large surface areas ranging from 373 m^2/g to 525 m^2/g and a mesoporous structure, indicating the promising potential of this material for application as a catalytic support.

Keywords: Pechini method; Characterization; Silica; Catalytic support

1. Introduction

Silica (SiO_2) is a ceramic material that is currently gaining prominence among the inorganic porous materials most widely used as catalyst supports [1]. Its importance is due primarily to the physicochemical properties that only an inorganic covalent structure can exhibit, such as high mechanical strength, high physical and thermal stability, high porosity, large specific surface area, and pore sizes ranging from micropores to mesopores [2].

A catalyst support is a material that constitutes the greater part of a catalyst and that serves as a base, support or binder of the active constituent (metal), but which alone has little or no activity in terms of the reaction in question. The function of a mechanical support is to serve as a base or structure for the catalyst component, which is the metal that acts as a catalytic promoting agent. In addition to this function, other desirable effects of a catalytic support are to increase the area exposed to the active agent, thereby augmenting the catalytic activity of an agent with low surface area; increase the stability of the catalyst; keep the crystals of the active material apart to prevent them from sintering and thus losing their activity; and to chemically complex the support with the active mass, resulting in higher activity per unit surface area [3].

The use of silica as a catalyst support in different chemical processes is widely reported in the literature. Nam et al. [4] evaluated commercial silica as a catalyst support for platinum/ruthenium, e.g., in the anode of methanol fuel cells, and compared its performance with that of a carbon black support with the same catalyst. The authors reported that the performance of the catalyst using a silica catalyst support at concentrations of 5 M of methanol with a maximum power density of 90 mW/cm^2 was threefold higher than that of the catalyst supported with carbon black, and that the silica particles had a significant effect in reducing the permeability of the electrolyte to methanol, and in controlling the methanol fuel supply.

Velan et al. [5] studied the effect of adding SiO_2 to the catalytic layer of the electrodes of a proton exchange membrane fuel cell (PEMFC). The Nafion membrane, which is used

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as electrolyte in the PEMFC system, has to maintain the system's hydration to ensure proton conductivity. For the stable operation of the reactant gas, the PEMFC system must be hydrated externally or internally to maintain the membrane's ionic conductivity. However, a high level of hydration causes flooding of the electrodes, which prevents or limits the supply of reactants to the catalyst. The authors found that the introduction of nanosilica in catalytic supports improved the control of hydration and the performance of the fuel cell.

Nihong et al. [1] used two types of commercial silica as support in platinum catalysts to evaluate the catalytic oxidation of formaldehyde. They reported that Degussa silica with a surface area of 390 m^2/g showed better performance than Qingdao silica in terms of catalytic activity, completely oxidizing the formaldehyde even at room temperature. The authors reported that the characteristics of silica supports affect the particle size and chemical state of platinum species, which in turn further influence the redox properties of Pt/SiO_2 catalysts.

Silica-based catalyst supports can be produced by different chemical synthesis methods. For example, Ren et al. [6] used the precipitation method, while Kesmez et al. [7], Rahim et al. [8], and Montes et al. [9] used the sol–gel method. The type of structure and morphology of the support can be altered depending on the method employed and the conditions of synthesis. Thus, it also affects the deposition of the metal or promoting agent, which in turn directly affects the catalytic activity of the catalyst in the chemical process to be tested.

This prompted our interest in synthesizing silica (SiO_2) by the Pechini method to produce nanoparticles with characteristics similar to commercially available ones, aiming to understand and expand the body of research using this material for application as an efficient and economically feasible catalytic support.

The choice of the synthesis method is a crucial step in obtaining nanoparticles, because the method must allow for better control of the specific surface area, smaller particle size, and low degree of agglomeration. In this context, the polymeric precursor method stands out among other chemical synthesis methods because it ensures reproducible chemical compositions, controlled particle sizes, stable structures and high purity [10–12].

This paper describes the preparation of nanosilica by the Pechini method and its structural and morphological characterization. The material was calcined from 600 °C/1h to 900 °C/1h to determine the effects of heat on the aforementioned characteristics.

2. Experimental

Nanosilica (SiO_2) was synthesized using the methodology proposed by Pechini [13], with a 3:1 M ratio of citric acid to metal cations. To this end, monohydrate citric acid ($C_6H_8O_7.H_2O$) and tetraethylorthosilicate (TEOS – $C_8H_2OO_4Si$) were mixed and stirred for about 24 h at 80 °C until they were completely dissolved, forming a homogeneous system. Ethylene glycol ($C_2H_6O_2$) was then added at a mass ratio of 40/60% in relation to citric acid and the mixture was heated to 100 °C to form a resin, which was pyrolyzed at 400 °C/1h, at a heating rate of 10 °C/min. The resin was then deagglomerated in an agate mortar, sifted through an ABNT #200 mesh sieve (74 μm) and calcined at 600 °C, 700 °C, 800 °C and 900 °C/1h at a heating rate of 10 °C/min.

After calcination, the nanosilica samples were characterized by X-ray diffraction (Shimadzu XRD-6000 diffractometer) using a monochromatic Cu-Ka radiation source of $\lambda = 1.54°$, a voltage of 40 kV and a current of 30 mA. Scanning measurements were taken in the range of 10° and 85° (2θ), using slits 1 (divergence slits: DS): 1 (spreading slits: SS): 0.3 (receiving slits: RS), applying a scan step of 0.02° (2θ). For the sieve analysis, the samples were sifted through a 325 mesh sieve (45 μm openings), dispersed in deionized water by ultrasound for 5 min, and then analyzed in a Malvern Mastersizer 2000 particle size analyzer. The texture analysis of the samples was performed using a Micromeritics GEMINI 2370 surface area and pore size analyzer. The specific surface area was determined by the BET method, which is based on the adsorption isotherm data in the range of relative pressure (P/P_0) from 0.05 to 0.30 [14]. Pore diameter and size distribution were determined by the BJH (Brunauer, Joyner and Halenda) method and the pore volume was determined based on the amount of nitrogen adsorbed at a P/P_0 of 0.95. This technique was also used to determine the average particle diameter (equivalent spherical diameter) using Equation 1 [15],

$$D_{BET} = \frac{6}{S_{BET}\rho} \quad (1)$$

where D_{BET} is the mean particle diameter (nm), S_{BET} is the specific surface area determined by the BET method (m^2/g), ρ is the theoretical density (g/cm^3), whose value for silica was 2.4 g/cm^3, and 6 is a factor calculated experimentally and adopted for smooth spherical particles. The morphology of the samples was analyzed by scanning electron microscopy (SEM, Shimadzu SuperScan SS500).

3. Results

Fig. 1 shows the X-ray diffractograms of the nanosilica samples. Note the presence of a broad band centered at around 22°, which characterizes the material as amorphous, i.e., without an organized crystalline structure. As can also be seen, increasing the calcination temperature from 600 °C/1h to 900 °C/1h did not affect the amorphous structure of the nanosilica, indicating the material's thermal stability. This amorphous characteristic was also reported by Nihong et al. [1] in his studies with commercial silica (Aerosil 380, Degussa) supported on platinum catalysts for the catalytic oxidation of formaldehyde (HCHO).

Table 1 describes the textural characteristics of the nanosilica samples. Note that the sample calcined at 600 °C, first calcination temperature, showed the highest specific surface area: 525.42 m^2/g, and as the calcination temperature increased the specific surface area decreased, resulting in increasing particle sizes, as expected. A comparison of the samples

calcined at 600 °C and at 900 °C/1h indicates that the specific surface area of the latter was 71% lower. On the other hand, the pore radius showed almost no variation, with values of about 20 Å, i.e., all the samples showed mesoporous characteristics (pore radius varying from 10 Å to 250 Å). The results indicate that, in terms of texture, the nanosilica samples consist of mesopores, presenting high specific surface areas and porosity.

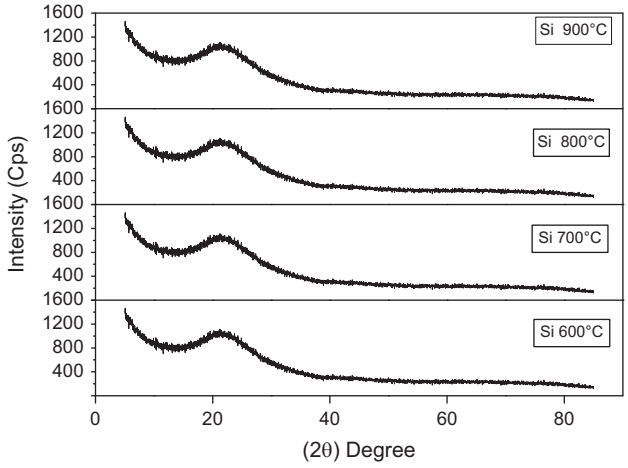

Fig. 1. X-ray diffractograms of samples prepared by the Pechini method and calcined at temperatures of 600–900 °C/1h.

The samples' specific surface areas were larger than the 380 m^2/g of the commercial silica (Aerosil 380, Degussa) [1]. The only exception was the sample calcined at 900 °C, whose specific surface area was very similar to that of the commercial sample.

Li et al. [16] used silica supplied by Sigma-Aldrich (Davisil, Grade 636) as support for palladium catalysts for the partial oxidation of methane to produce synthesis gas. After oven-drying at 110 °C/24h, their sample showed a specific surface area of 430 m^2/g, a pore volume of 0.88 cm^3/g and a mean pore diameter of 64.4 Å. After calcination at 800 °C/2h, the specific surface area was 433 m^2/g, pore volume was 0.85 cm^3/g and mean pore diameter was 64.2 Å. A comparison of Li et al.'s data with those of the nanosilica samples calcined at 800 °C in this work indicates that the textural characteristics were similar, presenting a difference of 14.56% in specific surface area, 37.93% in pore

Table 1
Specific surface area, particle diameter, and pore volume and diameter of the samples prepared by the Pechini method and calcined at 600–900 °C/1h.

Samples	(BET) (m^2/g)	(D_{BET}) (nm)	Pore volume (cm^3/g)	D_P (Å)
Si 600	525.42	4.6	0.5445	41.55
Si 700	488.94	5.0	0.5081	41.61
Si 800	369.98	6.6	0.5276	38.69
Si 900	373.30	6.5	0.3878	41.55

Table 2
Agglomerate sizes of the silica samples prepared by the Pechini method.

Sizes of agglomerates	Si 600 °C (μm)	Si 700 °C (μm)	Si 800 °C (μm)	Si 900 °C (μm)
a 10%	5.1	5.6	4.7	4.8
a 50%	30.9	36.5	28.3	32.6
a 90%	78.2	84.0	73.2	78.5

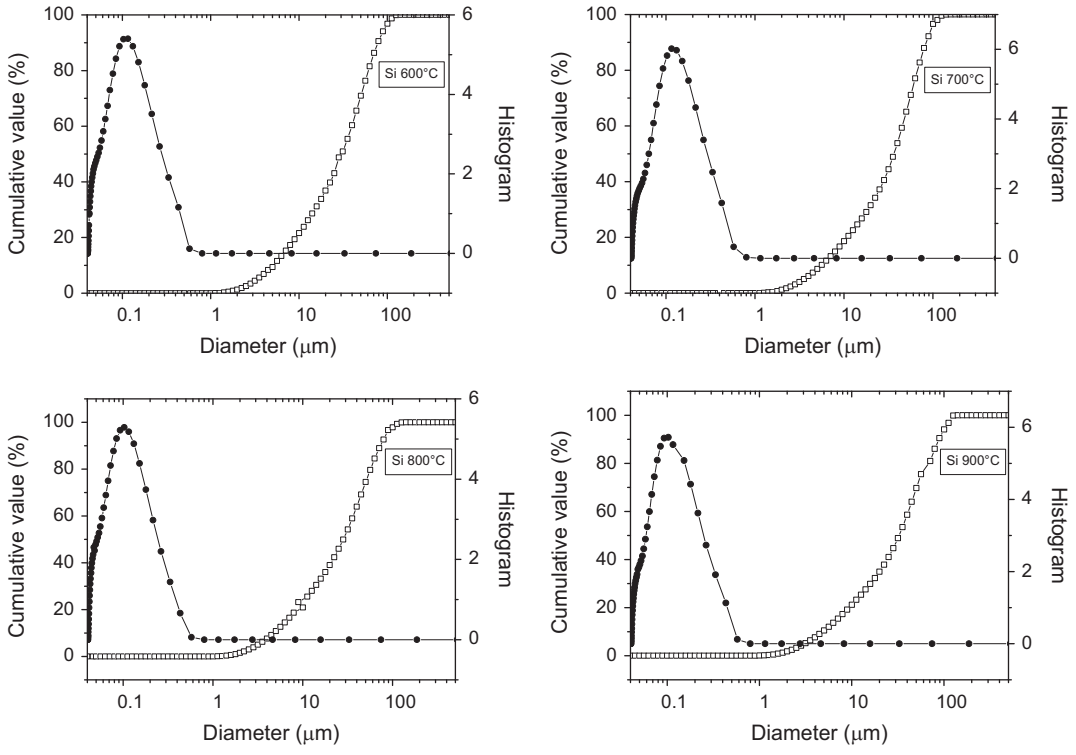

Fig. 2. Particle size distribution curves of the samples prepared by the Pechini method and calcined at temperatures of 600–900 °C/1h.

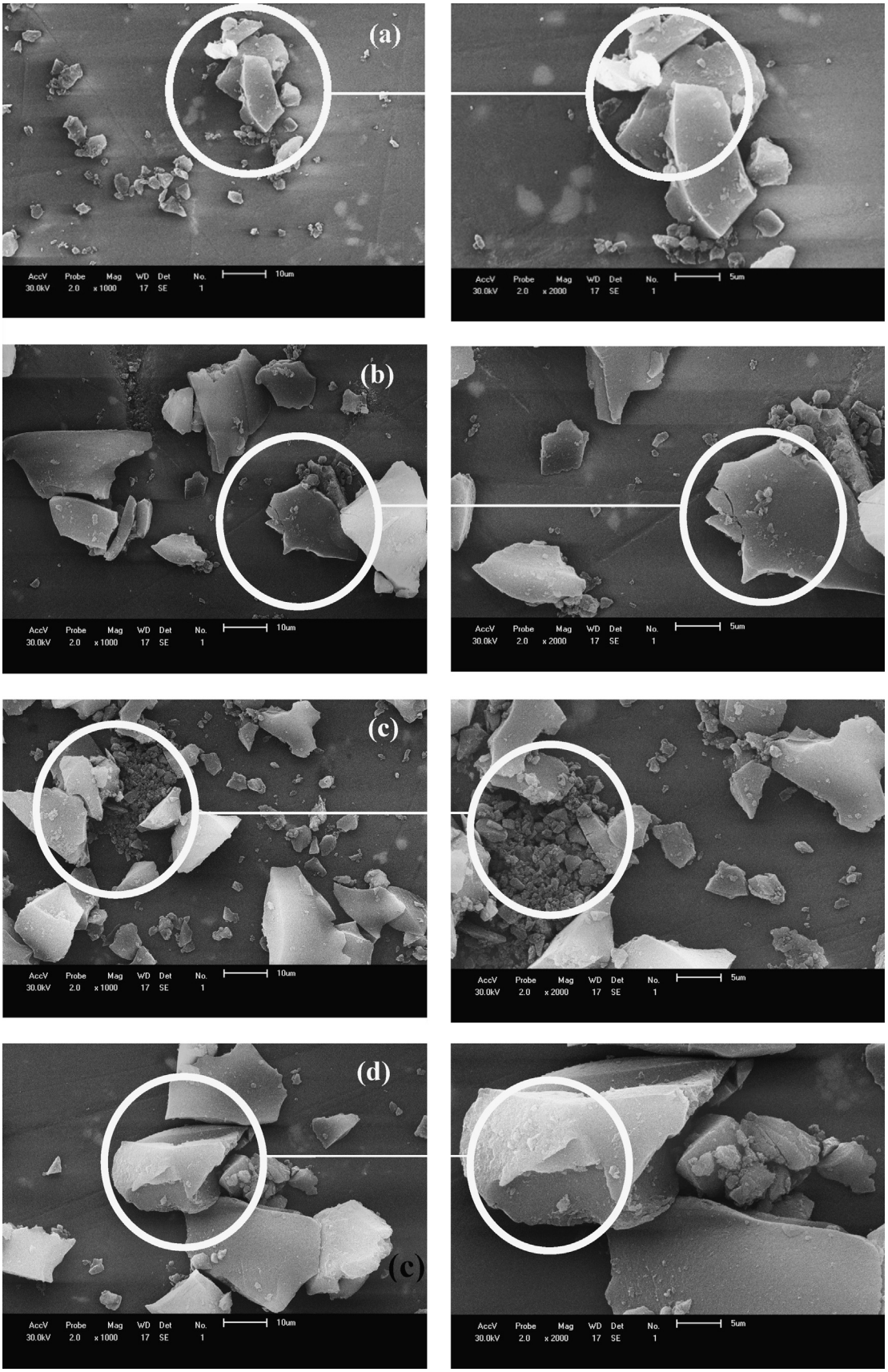

Fig. 3. SEM micrographs of samples prepared by the Pechini method at: (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C/1h.

volume, and 40% in pore diameter in relation to the commercial silica.

Fig. 2 shows the particle size distribution curves of equivalent spherical diameter of agglomerates as a function of cumulative weight of the samples prepared by the Pechini method and calcined at temperatures of 600 °C/1h to 900 °C/1h. As can be seen, in all the analyzed temperature conditions, the samples showed the same curve profile, with a narrow monomodal agglomerate size distribution. Therefore, increasing the calcination temperature did not affect in the agglomerate size distribution of samples prepared by the Pechini method.

Table 2 lists the sizes of agglomerates in the proportions of 10, 50 and 90% of cumulative mass. Note that agglomerate sizes in the aforementioned proportions were very similar at all the calcination temperatures. At a proportion of 10%, the agglomerate sizes varied from 4.7 μm to 5.6 μm, while at the proportion of 50% they varied from 28.3 μm to 36.9 μm, and at the proportion of 90% they ranged from 73.2 μm to 84.0 μm.

Fig. 3(a–d) shows SEM micrographs of the samples prepared by the Pechini method and calcined at temperatures of 600 °C/1h to 900 °C/1h. The morphology of all the samples consisted of rigid irregular plate-shaped agglomerates, albeit composed of fine interconnected particles, which explains the presence of mesopores and the high specific surface areas (Table 1). Increasing in the calcination temperature from 600 °C to 900 °C was found not to alter the samples' morphology. In addition, a narrow agglomerate size distribution was observed, with agglomerates smaller and larger than 38 μm, confirming the results shown in Fig. 2.

4. Conclusions

The Pechini method proved to be a simple and efficient synthesis method for producing nanosilica with amorphous mesoporous structure and high thermal stability, which was confirmed by the fact that increasing the calcination temperature from 600 °C to 900 °C did not alter the structure of the samples. With regard to their morphology, the samples were composed of irregular plate-shaped agglomerates with a narrow size distribution. The samples' high specific surface areas of 373.30 m^2/g to 527.42 m^2/g suggests that nanosilica produced by the Pechini method, in all the conditions evaluated here, is a promising material for application as a catalyst support for metals, and is comparable to the commercial silica evaluated in several studies reported in the literature.

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