

Preparation and characterization of mesoporous Titanium-silica and zirconia-silica mixed oxides

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(Recibido: 10 de enero de 2006; Aceptado: 13 de mayo de 2006)*

An experimental strategy was developed to obtain mesoporous SiO₂-ZrO₂ and SiO₂-TiO₂ mixed oxides via the sol-gel process. SiO₂-ZrO₂ materials involved the use of tetraethylorthosilicate (TEOS) and an inorganic Zr-containing salt source (nitrate). The ZrO₂ content, the synthesis pressure on the solids properties were studied and further modification of this type of procedure. In the case of the SiO₂-TiO₂ materials were synthesized by a sol-gel method using tetraethylorthosilicate (TEOS) and titanium isopropoxide, in a typical preparation. Both precursors were dried and calcined at 500°C. The solids were characterized by nitrogen physisorption, pyridine chemisorption, ²⁹Si Nuclear Magnetic Resonance, SEM and X-ray diffraction. Characterization of the solids revealed that mesoporous materials with very narrow pore diameter distribution were obtained when using the autoclave procedure from both mixed oxides. Surface areas and pore size distribution were a function of ZrO₂ and TiO₂ content. Differences in acidity as determined by pyridine adsorption were observed depending on the synthesis parameters.

Keywords: Modified Silica, Zirconia, Titania, mixed oxides; BET surface measurements.

1. Introduction

Silica is a naturally occurring material in minerals, such as quartz and flint, and in plants such as bamboo, rice and barley. The properties of silica have been extensively studied by many authors, due to its wide range of applications [1,2]. Combinations of silica with a large number of other oxides have been reported [3]. Pure ZrO₂ and TiO₂ carriers have very small specific surface area, low thermal stability and high price, that makes them unsuitable for industrial applications. In order to overcome these drawbacks, increasing attention has been paid to the development of mixed oxide supports by combining the higher surface areas and thermal stability of silica with the unique acidic properties of ZrO₂ and TiO₂. Mixed titania-silica and zirconia-silica materials are potentially useful in a number of technological applications, including catalyst. More particularly, previous work has been published on the silica-zirconia system as synthesized by the sol-gel method [1,4]. However, it is necessary to shed light on several issues concerning the synthesis and characterization of this system by using the sol-gel method. SiO₂-ZrO₂ mixed oxides have gained increasing attention in recent years because of their interesting characteristics and many applications, which include alkali-durable glasses [5], catalyst support [6,7] and as an advanced ceramic material [8]. Comparison of the various results in the literature is

sometimes difficult because of different preparation methods, sample treatments, or characterization techniques used to determine the structural and surface properties. In spite of this situation we will try to provide a consistent picture in order to clarify structure-property relationships in silica-zirconia materials based on the combined results of different characterization techniques such as x-ray powder diffraction, N₂ physisorption, ²⁹Si NMR spectroscopy and FTIR pyridine thermodesorption. The representative methods of preparation of porous materials in the SiO₂-ZrO₂ system are using a sol gel method [9], although the literature related to the synthesis of SiO₂-ZrO₂ is very scarce. The starting components are usually alcoholic solutions of alkoxides which undergo condensation reactions after initial hydrolysis. The homogeneous incorporation of Zr into a matrix is important to obtain materials that exhibit chemical, thermal and mechanical stabilities. The goal of the present work was to obtain mesoporous SiO₂-ZrO₂ and SiO₂-TiO₂ systems, based on a controlled hydrolysis-condensation process. The experimental strategy developed here allows one to obtain mesoporous materials when the gel is treated in an autoclave and heated to 150°C. Previous works in our group have pointed out the importance of a fine tuning of the synthesis conditions in order to produce solids with the desired characteristics [10]. In view of the acidic properties

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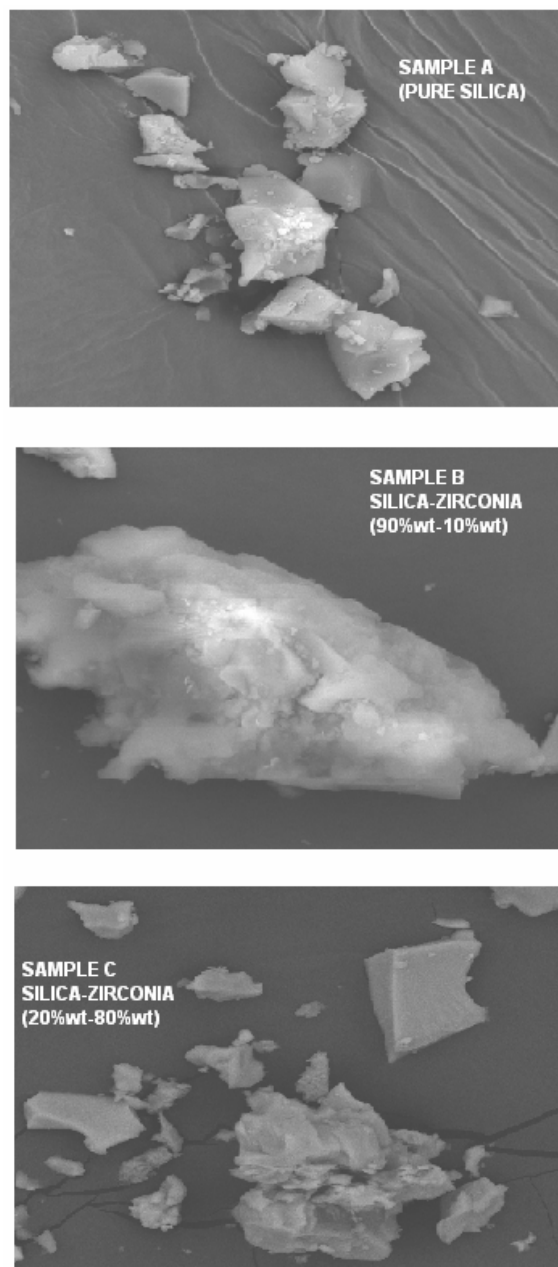


Figure 1. Typical SEM photographs of $\text{SiO}_2\text{-ZrO}_2$ with different SiO_2 content calcined at 550°C . (A) Pure silica, (B) Si-Zr (90-10) with autoclave, (C) Si-Zr (20-80) with autoclave.

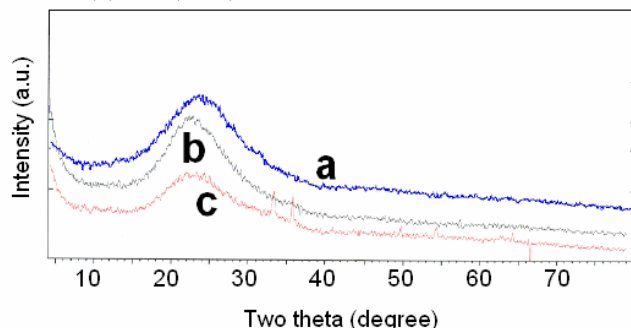


Figure 2. XRD patterns of porous $\text{SiO}_2\text{-ZrO}_2$ with high SiO_2 content calcined at 550°C . (a) Pure silica, (b) Si-Zr (80-20) with autoclave, (c) Si-Zr (60-40) with autoclave.

of $\text{SiO}_2\text{-TiO}_2$ systems demonstrated by Ithot et al. [11], then we decided to use them as supports to compare them with TiO_2 to see how TiO_2 in different environments would affect the interaction.

2. Experimental Section

2.1 $\text{SiO}_2\text{-ZrO}_2$ Synthesis

The materials were synthesized by a sol-gel method, using tetraethylorthosilicate (TEOS) (Aldrich) as the SiO_2 source, an inorganic Zr-containing salt ($\text{ZrO}(\text{NO}_3)_2$, Aldrich), as the ZrO_2 source, water as solvent and nitric acid as hydrolysis catalysts. In a glass reactor, TEOS was dissolved in 300 ml of water at 85°C . The mixture was maintained under vigorous stirring for 30 minutes and an aqueous solution of the Zr(IV) salt was added dropwise at 85°C to achieve $\text{ZrO}_2\text{:SiO}_2$ weight ratios of 0:100, 20:80, 40:60, 60:40 or 80:20. Stirring was continued for 120 min to promote hydrolysis and condensation. After condensation, the resulting gel was placed in an autoclave and heated at 150°C for 24 h. The resulting precursors were carefully dried and calcined in flowing air at 550°C . Samples were named in terms of the zirconium oxide concentration, i.e. Si-Zr (90-10) corresponds to a materials containing 90wt% SiO_2 and 10wt% ZrO_2 etc.

2.2 $\text{SiO}_2\text{-TiO}_2$ Synthesis

Titanium isopropoxide and tetraethylorthosilicate (TEOS) were used as titanium precursor and silica source, respectively. TEOS was added to nitric acid solution at 85°C with magnetic stirring after 25 minutes a clear solution was formed. Titanium isopropoxide was then added dropwise to the above solution under magnetic stirring within 30 minutes to form a sol. Then the gel was loaded into an autoclave at 150°C for 24 h. The product was dried and calcined in air at 500°C to obtain silica-titania mixed oxides. Samples were named in terms of the titanium oxide concentration, i.e. Si-Ti (90-10) corresponds to a materials containing 90wt% SiO_2 and 10wt% TiO_2 etc.

2.3 Characterization

All materials were calcined at 500°C , they were characterized by XRD, N_2 physisorption, SEM and their acid properties were analyzed by TPD of pyridine. The powder X-ray diffraction patterns were measured on a Siemens D-500 diffractometer with a graphite secondary beam monochromator, and the $\text{CuK}\alpha_2$ contribution was eliminated by DIFFRAC/AT software ($\text{CuK}\alpha$ radiation with $\lambda = 1.5406 \text{ \AA}$). Adsorption measurements were performed in a volumetric apparatus equipped with pressure and vacuum detectors. Increasing amounts of adsorbate were added until saturation. Surface areas, pore size distributions, and pore volumes were measured by nitrogen adsorption at 75 K using Micromeritics Accusorb 2100 E

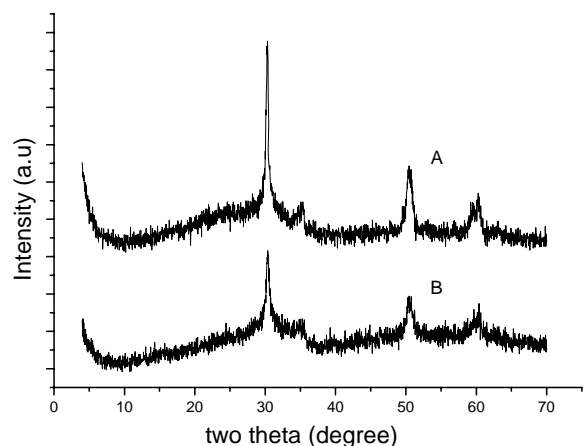


Figure 2a. XRD patterns of porous $\text{SiO}_2\text{-ZrO}_2$ with high ZrO_2 content calcined at 550°C . (A) Si-Zr (60% -40%) precursor: cloruro con autoclave: SZ(VI)-CA (B) Si-Zr (20% -80%) con autoclave: SZ(VII)-CA.

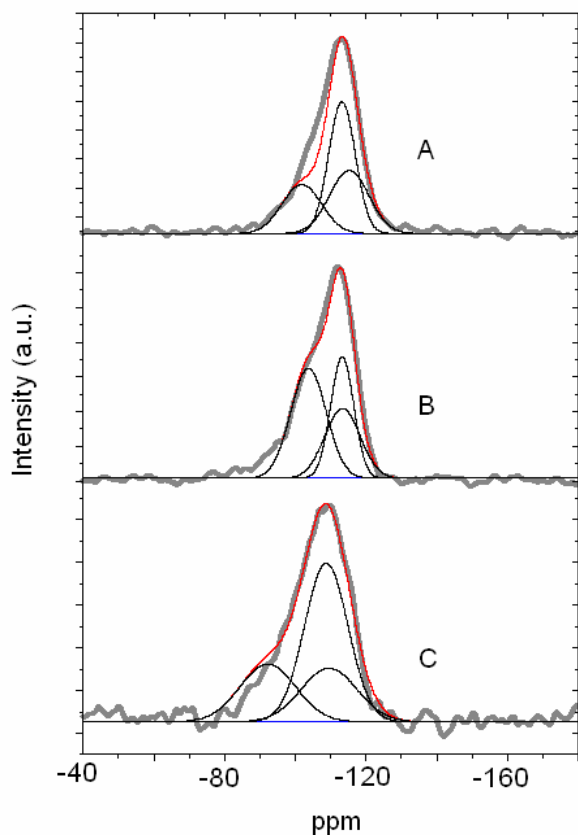


Figure 3. ^{29}Si NMR deconvolution of $\text{SiO}_2\text{-ZrO}_2$ with different ZrO_2 content calcined at 550°C (A) Si-Zr (90-10) with autoclave, (B) Si-Zr (80-20) with autoclave, (C), (E) Si-Zr (20-80) without autoclave.

equipment. The surface area was calculated with the BET method and the pore distribution with the BJH model.

Before the analysis, the samples were treated at 300°C under vacuum. ^{29}Si NMR spectroscopy was performed to study the changes in the SiO_2 structure when Zr atoms are incorporated into the silica network (Bruker). The materials were characterized by FTIR pyridine thermodesorption on a Perkin Elmer Apparatus.

3. Results

Morphology and X-Ray Diffraction

The morphology and the long-range order were investigated by scanning electron microscopy and X ray powder diffraction. Typical SEM photographs are given in Fig. 1. It can be seen that there is a modification with the zirconia addition in the morphology which corresponds to aggregates without regular shapes.

X-ray diffraction patterns were obtained for the calcined samples at several ZrO_2 contents. Fig. 2 shows the amorphous diffraction patterns for samples with high SiO_2 content (pure silica, Si-Zr (80-20) with autoclave, Si-Zr (60-40) with autoclave), even those calcined at 500°C , whereas those corresponding to the samples dried in an autoclave at high ZrO_2 content were crystalline (monoclinic ZrO_2). The patterns were compared to JCPDS files. For the samples with high ZrO_2 content it is interesting to note that the tetragonal or cubic phases were observed.

By contrast, the samples of $\text{SiO}_2\text{-TiO}_2$ prepared with high SiO_2 content were amorphous. It was clear that crystallization of mixed oxides of silica-zirconia was observed when the added amount of ZrO_2 was increased. Extensive crystallization seemed to occur in the samples Si-Zr (40-60) and Si-Zr (20-80).

^{29}Si NMR spectroscopy

Experiments were performed with a high resolution solid state NMR spectrometer (Bruker, model 400). The ^{29}Si spectra were recorded at room temperature at a frequency of 79.4 MHz. Samples were spun at the magic angle using a frequency of 10 KHz. ^{29}Si shows chemical shift for the observable resonances of the silica surface. In the sample Si-Zr (90-10) resonance corresponds to species with three siloxane bonds and one hydroxyl group (silanol sites), when the content of ZrO_2 is increasing resonance corresponds to surface silicon atoms with four siloxane attachments (interconnecting lattice sites), and resonance due to silicon atoms with two siloxane bonds and two hydroxyls (silanediol sites) as shown the deconvolution in Fig. 3. The presence of Si-O-Zr bonding in $\text{SiO}_2\text{-ZrO}_2$ mixed oxides has been detected indirectly

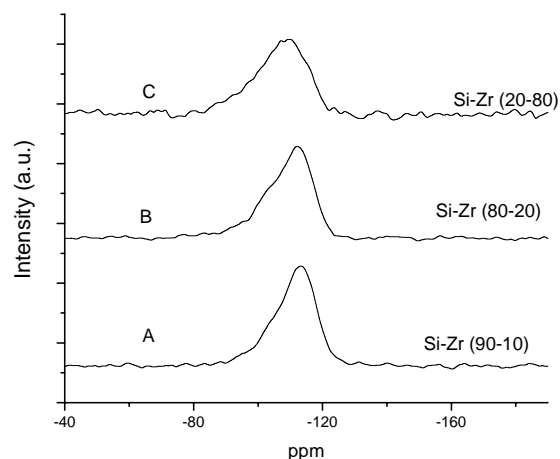


Figure 3a. ^{29}Si NMR of $\text{SiO}_2\text{-ZrO}_2$ with different ZrO_2 content calcined at 550°C (A) Si-Zr (90-10) with autoclave, (B) Si-Zr (80-20) with autoclave, (C), (E) Si-Zr (20-80) without autoclave.

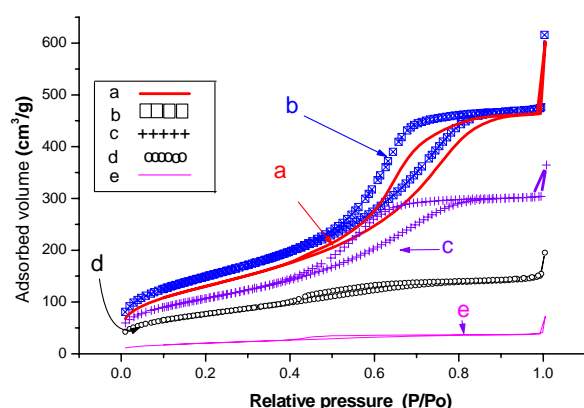


Figure 4. Nitrogen adsorption-desorption isotherms for $\text{SiO}_2\text{-ZrO}_2$ mixed oxides with different Zr content. (a) Silica pure, (b) Si-Zr (90-10), (c) Si-Zr (80-20), (d) Si-Zr (40-60), (e) Si-Zr (20-80). All the samples were put into an autoclave.

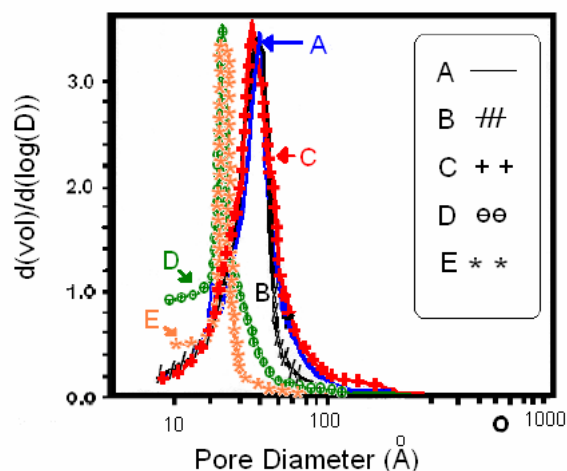


Figure 5. Pore size distributions of Si-Zr samples with different content of Zr, calcined at 550°C . (A) Pure silica with autoclave, (B) Si-Zr (90-10) with autoclave, (C) Si-Zr (80-20) with autoclave, (D) Si-Zr (40-60) without autoclave, (E) Si-Zr (20-80) without autoclave.

by ^{29}Si NMR spectroscopy (Fig. 3a). From XRD and NMR, two types of Zr species are present in $\text{SiO}_2\text{-ZrO}_2$ mixed oxides: segregated ZrO_2 microdomains and isolated Zr species, with the relative ratio depending on the chemical composition, the preparation methods, synthesis conditions (the hydrolysis route, Zr content, drying method and calcination temperature).

In $\text{SiO}_2\text{-TiO}_2$ mixed oxides the degree of homogeneity at the atomic level is commonly associated with the relative amount of Si-O-Ti linkages in $\text{SiO}_2\text{-TiO}_2$ mixed oxides, and Si-O-Ti bonds are more effectively formed as the homogeneity increase.

N_2 Physisorption

N_2 adsorption – desorption isotherms for the silica-zirconia mixed oxides are given in Figure 4. For all samples dried at atmospheric pressure type I isotherms were obtained [12]. The results indicate that microporous materials were obtained. The low hysteresis in the desorption branches can be interpreted as the existence of smooth and cylindrical pores [12].

On the other hand, the samples that were treated in the autoclave have adsorption isotherms of type IV, according to IUPAC classification. It is observed that the low relative pressure point, where the adsorption and desorption branches coincide, is affected by the ZrO_2 content of the sample.

Hysteresis appears at higher relative pressures, indicating the occurrence of capillary condensation in larger pores. This is confirmed by the pore size distribution (PSD) curves that were obtained from the desorption isotherms; see Fig. 5.

This figure shows that the PSDs are unimodal and move toward larger pores when increasing the SiO_2 content of the sample. The BET surface area, pore volume (V_p), average pore diameter for the $\text{SiO}_2\text{-ZrO}_2$ mixed oxides are given in Table 1.

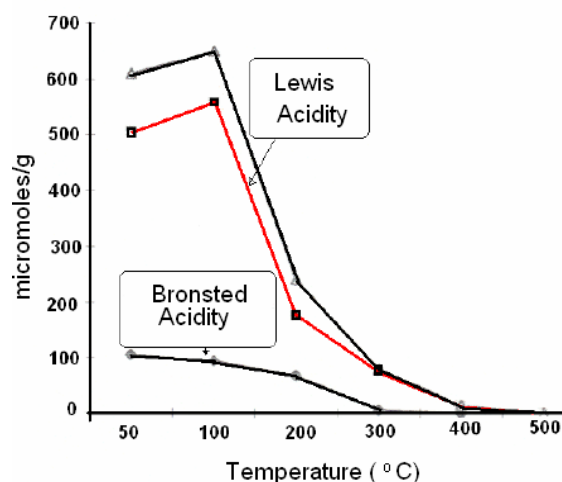
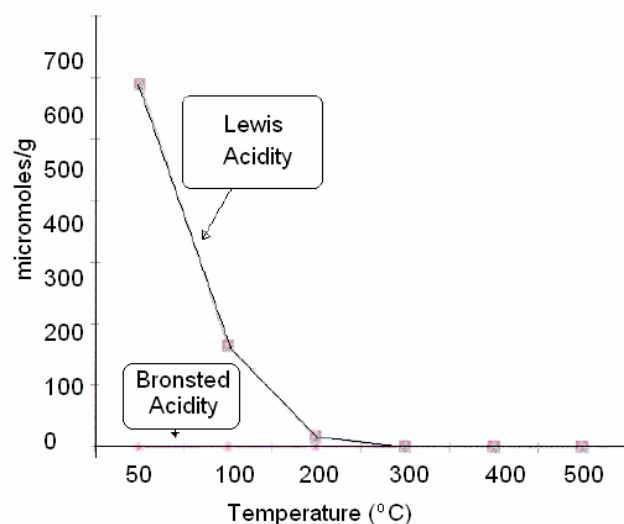
Pyridine adsorption

The adsorption of pyridine on the supports prepared was performed to obtain the acidity of the surface. The amounts of pyridine adsorbed are plotted in Figures 6, 7. The results show two different trends for the two systems; the mixed oxides showed Lewis sites and Brönsted sites for the primary synthesis while only Lewis sites were present for the hydrothermal synthesis.

Our results indicate that upon primary synthesis the materials increase their acidity, in other words, the kind of acid site is modified with the environment of the autoclave. The results on this system (Si/Zr) could be explained in terms of the structural modifications that the inclusion of ZrO_2 brings about.

Table 1.- Influence of the synthesis parameters on the texture.

| SAMPLE | S_g^a (m ² /g) | ϕ_p^b (Å) | V_p^c (cm ³ /g) | Region |
|---|-----------------------------|----------------|------------------------------|--------------------|
| Si-Zr (90-10) nitrate without autoclave | 270 | 23 | 0.14 | Transitional pores |
| Si-Zr (90-10) nitrate with autoclave | 481 | 79 | 1 | Mesopores |
| Si-Zr (90-10) chloride with autoclave | 374 | 83 | 0.77 | Mesopores |
| Pure silica with autoclave | 412 | 91 | 0.93 | Mesopores |
| Si-Zr (90-10) chloride with autoclave | 374 | 83 | 0.77 | Mesopores |
| Si-Zr (80-20) chloride with autoclave | 343 | 66 | 0.56 | Mesopores |
| Si-Zr (60-40) chloride with autoclave | 430 | 57 | 0.5 | Mesopores |
| Si-Zr (40-60) chloride with autoclave | 247 | 49 | 0.3 | Mesopores |
| Si-Zr (20-80) chloride with autoclave | 66 | 68 | 0.1 | Mesopores |

^a: Surface area^b: Pore volume^c: Average pore diameter**Figure 6..** Pyridine chemisorption of SiO₂-ZrO₂ with primary synthesis method, nitrate and calcined at 550°C.**Figure 7.** Pyridine chemisorption of SiO₂-ZrO₂ with hydrothermal synthesis method, nitrate and calcined at 550°C.

4. Conclusions

SiO₂-ZrO₂ and SiO₂-TiO₂ have been prepared by the sol-gel method. The results reported in this work clearly indicate that sol-gel methods can be a viable way to prepare mesoporous SiO₂-ZrO₂ and SiO₂-TiO₂ mixed oxides. Variations in the synthesis conditions produced solids of different characteristics. It was found that the ZrO₂ content influences the texture, structure and morphology of the samples. It was found that zirconia-silica (ZrO₂-SiO₂) calcined at 500°C exhibited no X-ray diffraction peak due to ZrO₂ in the content region from 0 %wt to 40 %wt; the Si-Zr oxides are in an amorphous state. Characterization of the solids revealed that mesoporous materials with very narrow pore diameter distribution were obtained when using the autoclave procedure. The textural properties were basically the same for the nitrate and chloride SiO₂-ZrO₂ samples. Structural and textural properties were similar for pure silica and silica-zirconia mixed oxides at Zr content < 40 wt %. When the gel was dried at atmospheric pressure the material exhibited pore diameters in the region of micropores. No difference in textural properties was observed in the primary synthesis and hydrothermal synthesis. However differences in acidity were obtained depending on the synthesis parameters.

Acknowledgements

R. G. Rodríguez Avendaño is grateful for a CONACYT (México) scholarship.

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