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The influence of AI_2O_3 content on AI_2O_3 -Zr O_2 composite-textural structural and morphological studies

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Abstract

In this work binary Al_2O_3 - ZrO_2 composites with 25, 50, and 75%, w/w Al_2O_3 were synthesized by the sol-gel method, to find out the better Al₂O₃ amount that improve the texture, structure, and morphology. The composites presented high surface area, porosity and microcrystalline structure due to high cations dispersion induced by a good intermingling of the components. We found that structure of Al_2O_3 - ZrO_2 composites include AlO₄ (tetrahedral), AlO₅ (pentahedral) AlO₆ (octahedral) polyhedral units. An increment of AlO₄ and AlO₆ species for low Al₂O₃ amount in the composites was observed. This was possibly related with segregated particles caused by progressive removal of hydroxyl groups. Otherwise, for high Al₂O₃ amount the fraction of AlO₅ species was high, this behaviour was associated with an appropriate distribution of cations within the network of the composites as derived from condensation reactions. A suitable distribution of the Al³⁺ and Zr⁴⁺ cations in the network of the composites is observable by Z-contrast where for high Al₂O₃ concentrations an homogeneous arrangement was observed. Besides, for low Al₂O₃ concentrations rods of ZrO₂ with an average length at ~250 nm are observable. Finally, by XPS analysis the non-lattice and lattice oxygen ratio presented similar values for Al₅₀Zr₅₀ composite, associated with the same available vacancies where Al³⁺ and Zr⁴⁺ cations have mayor mobility in the bulk and the superficial of the composite.

1. Introduction

The synthesis of materials from metal-organic precursors, such as metal alkoxides, allow the mixing of components at molecular level. Different parameters during the sol-gel process provide a new approach to the preparation of new materials. This process can give suitable control of the whole reactions involved during the synthesis of materials. Homogenous multi-component systems can be easily obtained by mixing the molecular precursors in solutions. This synthesis modified the structure, texture, and morphology of the final material. The attractive possibilities of these materials provide: high purity, molecular level homogeneity in multicomponent materials, particle size between 20 to 50 Å, and high reactivity [1].

Sol-gel method has attracted attention in various areas of research and it used as anticorrosive [2], films hybrids [3] as catalysts [4] as dielectric glass [5] and other areas with good results. The sol-gel technique offers the possibility to control characteristics through the modification of synthesis procedure, including changing the functionality of the metal-organic precursors, where reactions oligomerization, complexation, among others are carried out during the synthesis [6].

The addition of hydrolysis and condensation catalysts, the amount of each metal-organic precursors and used different solvents generates significant structural changes in the final product [7]. Acids and bases have been employed as catalysts during the sol-gel synthesis, which affected the texture and structure properties generated mixed oxides [8, 9]. During the synthesis of materials by sol-gel are usually employed several kinds of catalysts, this promotes different reactions between the precursors, which was affected the final physicochemical properties. The use of acids in the sol-gel synthesis is very common, because they act as catalyst in the hydrolysis reactions of the alkoxide precursors, promoting moderate surface areas and low pore volumes. Otherwise, when basic catalysts are used they promote the hydrolysis and condensation reactions during the sol-gel synthesis. These condensation reactions formed chains due to the generation of labile bonds in the terminal groups of the alkoxide precursors. This generates a degree of cross-linking between the chains of the precursors and the elimination of water molecules. For example the use of NH₄OH as catalyst allows the generation of agglomerates with low energy and improvement the textural and structural properties and possibly generated high porosity associated with a thermal shock resistance [10].

Previous works have focused on textural and structural changes due to the use of different solvents and additive of synthesis for Al_2O_3 - TiO_2 [11, 12] and Al_2O_3 - ZrO_2 [13, 14] systems. The interactions of these systems with different solvents or additive of synthesis affects the properties of the final materials. Other variation during the synthesis changed the amount of each metal-organic precursors [15–18], where the stability of system is given by tetragonal zirconia phase within Al_2O_3 matrix [19]. The tetragonal to monoclinic transition started in the surface and progress into the material bulk, also reduce the grain size and increase the concentration of the oxide, making a popular alternative to stabilizer mixed composites because it proved a high fracture toughness and strength [20]. Pure ZrO₂ cannot be used for fabricated ceramic forms without stabilizers additions [21], this has also been used in coating, glasses and films [22].

The change in the concentration of one of the precursors will generate modifications in its textural, structural and morphological properties. Li *et al* [23], synthesized two series of Al_2O_3 - ZrO_2 powders with various contents of ZrO_2 via sol-gel and co-precipitation methods. Where the use of a sol-gel method was related to more homogeneous powders and retardation in the aggregation of particles than co-precipitation method, observed by TEM, SEM and X-ray diffraction analysis. The zirconia incorporation into alumina, affected the surface properties of the powders upon heating exerting a protective effect against sintering and this inhibited the crystallization of the γ -A1₂O₃ phase and the transformation from γ - to α -phase, where the transition of zirconia is dispersed in alumina matrix and does not form a new structure [24]. The mixture of Al_xZr_{1-x} composites offers the possibility of a compromise among these mechanical properties with low toughness. This typical mechanical property of the material is associated with glass and ceramic bodies that prevent the crack propagation [25].

Furthermore, a decrease in the zirconium amount showed fully crystalline phases and the amount of t-ZrO₂ phase increased. In this case, an isolation effect could happen owing to the positioning of t-ZrO₂ particles within the Al₂O₃ matrix [25–28]. Also, for nanoparticles of Al₂O₃-ZrO₂, it is well known that the high ZrO₂ content improves the dispersion and the mechanical properties of Al₂O₃-ZrO₂ ceramics than Al₂O₃ monolithic. ZrO₂ could inhibit the sintering of Al₂O₃ this is due that the homogeneous distribution of ZrO₂ for several dispersion methods are extremely important [29].

The aim of this work, was to determine the Al_2O_3 concentration effect on the textural, structural and morphological properties of Al_xZr_{1-x} composites synthesized via sol-gel. Similar systems have been studied previously by this technique and acids are commonly used as synthesis additives. These additives promote hydrolysis reactions which involve the splitting of a bridging by a water molecule yielding by group hydroxyl between the precursors. However, our study is based on the change of physicochemical properties, starting from the change of concentration of one of the precursors. In addition, we investigated the use of a basic catalyst that promoted the condensation reactions between the alkoxides precursors.

2. Experimental

2.1. Synthesis of $Al_x Zr_{1-x}$ composites

The binary Al_xZr_{1-x} composites with different Al_2O_3 concentration (named as Al_xZr_{1-x} , where x is the Al_2O_3 % w/w = 25, 50, and 75) were synthesized by sol-gel technique as described by Escobar *et al* [12]. This process undergoes in few steps to obtain the final composite by hydrolysis, condensation reactions and a drying process.

The formation of metal oxides involves different consecutive steps, initially the corresponding metal precursor undergoes rapid hydrolysis to produce the metal hydroxide solution, followed by immediate condensation which leads to the formation of three-dimensional gels. Aluminum-tri-sec-butoxide [Al(OCH(CH₃)C₂H₅)₃, 99.9%] and zirconium (IV) propoxide [Zr(OCH₂CH₂CH₃)₄, 70%] were used as alkoxides precursors, both were mixed in 2-propanol ((CH₃)₂CHOH, 99.5%; 278K) at 300 rpm stirring. Ammonium hydroxide aqueous solution (NH₄OH, 28%) was used as a synthesis additive and it was added dropwise to the alkoxide-alcohol mixture. The resulting gels were aged unstirring for 24h at 278K for its subsequent drying vacuum at 333K and then, calcining at 773K for 5h in static atmosphere. A heating rate at 5 K \cdot min⁻¹ was used each time. The alcohol/alkoxide, H₂O/alkoxide and additive/alkoxide molar ratios were 65, 20 and 0.2, respectively. Sigma-Aldrich provided the reactants above.

2.2. Characterization

The textural properties of the composites were measured by Nitrogen Physisorption using an Autosorb I (Quantachrome) equipment. All composites were degassed at 673 K to a vacuum pressure at 6 μ mHg. The BET equation was used to calculate surface area (Sg) and pore volume (VP) by Barrett–Joyner–Halenda (BJH) method was applied to the desorption profile-branch of the nitrogen isotherm. The Al_xZr_{1-x} composites were analysed in a D-500 Siemens diffractometer, with radiation CuK_{α} ($\lambda = 0.15406$ Å) using a nickel filter with 35 KV, 20 mA and scanning rate at 0.001°.

The structural properties of the composites were measured by ²⁷Al magic angle spinning-nuclear magnetic resonance in an Avance-II 300 Bruker spectrometer, operating at ¹H frequency at 300 MHz (7.05 Tesla), ²⁷Al frequency at 78.15 MHz, ZrO₂ with 4 mm external diameter rotor, spinning rate at 10 KHz and radio frequency pulses at 2.0 μ s, using Al(H₂O)₆³⁺ was the external reference. Besides, the chemical analysis was obtained using X-ray photoelectron spectroscopy (XPS), using a microprobe PHI 5000 VersaProbe II, with an AlK α x-ray source ($h\nu = 1483.6$ eV). The surface of samples etched for 2 min with 3.0 kV with Ar⁺ at 0.06 μ A mm⁻². The XPS spectrum was obtained at 45° to the normal surface in the constant pass energy mode (CAE), E₀ = 117.4 and 11.75 eV for survey and high-resolution narrow scan, respectively. The peak positions were referenced to the background silver *Ag 3d*_{5/2} photo-peak at 368.20 eV, having a Full Width at Half Maximum (FWHM) at 0.56 eV, *Au 4f*_{7/2} in 84.00 eV and *C 1s* hydrocarbon groups in 285.00 eV central peak position. The XPS spectra were fitted with the program SDP v4.1, the recorded spectra were fitted through a Gaussian–Lorentzian combination based on an Offset Shirley background type [30].

Finally, the morphological analysis for Al_xZr_{1-x} composites was determined by scanning electron microscopy using a JEOL 7600F equipment, with secondary electron radiation at magnification resolution 30000 x and 15000 x with 7.4 mm work distance and low energy 35 eV. The images of *Z*-contrast were obtained in a JEOL JEM-2100F equipped with a STEM unit, HAADF and bright field (BF) detectors. Additionally, the resolution in HAADF/BF-STEM modes was of the order of 0.2 nm. The potentialities of HADDF detector imaging provided a direct interpretable atomic number, *Z*-contrast showed information for atomic density images by weight. Thus, the small bimetallic distribution of Al-Zr cations was observed.

3. Results and discussion

3.1. Textural properties

3.1.1. Nitrogen physisorption

The Al₂O₃ amount into Al_xZr_{1-x} composites modified the adsorption-desorption isotherms, as determined by Nitrogen Physisorption. The N₂ adsorption-desorption isotherms are giving in figure 1. The variation of *x* into Al_xZr_{1-x} composites modified the N₂ adsorption-desorption isotherms significantly, suggesting important modifications in the mesoporous networks of the Al_xZr_{1-x} composites. According to the IUPAC classification [31], all materials exhibited a type IVa adsorption isotherm along with hysteresis loops, although significant differences in the hysteresis loop type were observed. First, the pure zirconia and alumina (x = 0 and 100 or Al_0Zr_{100} and $Al_{100}Zr_0$; see inset of figures 1(a) and (e)) shows a type H2b hysteresis loops related to the formation of pores with relatively uniform channel-like pores with connectivity between them. Subsequently, $Al_{25}Zr_{75}$ and $Al_{75}Zr_{25}$ composites (figures 1(b) and (d)) displayed type H3 hysteresis loops, typically related to aggregates of plate-like particles forming slit-like pores. A type H4 hysteresis loop indicative of particles with internal voids of irregular shape and broad size distribution forming narrow slit-like pores was obtained for the $Al_{50}Zr_{50}$ composite.

 Al_xZr_{1-x} materials with at least 25 w/w, % Al_2O_3 (x > 25) reached substantial increases in surface area (S_g) and pore volume (V_P), but with a decrease of around 64% in pore diameter (D_P) value (table 1). Approximately 7- and a 10-fold increase in the S_g and V_P value where obtained when Al_2O_3 fraction was increased from x = 0 (pure zirconium or A_0Z_{100} , 43 m² · g⁻¹ and 0.12 cm³ · g⁻¹) to x = 25 ($Al_{25}Zr_{75}$; 317 m² · g⁻¹ and 1.22



 Table 1. Textural measured properties of Al₂O₃-ZrO₂ composites.

Composite	Al_2O_3	Sg	V_P	D_P
		$\pm 10\%$	$\pm 5\%$	$\pm 3\%$
	$(w w^{-1})$	$(m^2 \cdot g^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	(nm)
Al ₀ Zr ₁₀₀	0	43	0.12	9.4
Al ₂₅ Zr ₇₅	25	317	1.22	3.4
$Al_{50}Zr_{50}$	50	329	0.76	3.8
Al ₇₅ Zr ₂₅	75	284	1.73	3.4
$Al_{100}Zr_0 \\$	100	273	0.75	9.4

cm³ · g⁻¹), respectively. For high Al₂O₃ concentration the S_g values reached a maximum value at x = 50 (329 m² · g⁻¹) and then decreased steadily with the Al₂O₃ content. Besides, two maximum V_P values were obtained at x = 25 and 75 w/w, % Al₂O₃ (1.22 and 1.73 cm³ · g⁻¹, respectively), while 0.76 cm³ · g⁻¹ was obtained for Al₅₀Zr₅₀ composite.



Finally, the mixed Al_xZr_{1-x} composites (x = 25-75) showed an equivalent decrease at 64% compared to Al_0Zr_{100} and $Al_{100}Z_0$ reference samples (both with $D_P = 9.4$ nm). The drastic decrease in V_P and D_P would be related to the loss of mesoporosity of the Al_xZr_{1-x} composites. $Al_{50}Zr_{50}$ presented higher $S_g = 329 \text{ m}^2 \cdot \text{g}^{-1}$ approximately 86% larger than Al_0Zr_{100} and the D_P (3.4–3.8 nm) are similar between $Al_{75}Zr_{25}$ and $Al_{25}Zr_{75}$ composites, these are approximately 61% smaller than Al_0Zr_{100} and $Al_{100}Zr_0$ usually used as reference samples (9.4 nm), all diameters were obtained within the range of mesoporous materials, which similar values have been reported by Soisuwan *et al* [32].

The increment of Al_2O_3 concentration in the composites generated the protonation of the alkoxide ligands that promoted the lability between the intermolecular bonds, generating a higher degree of reticulation than reference samples. These generated different textural properties due to the formation of small size agglomerates with S_g and V_P moderately higher with respect to the Al_0Zr_{100} and $Al_{100}Zr_0$ samples.

3.1.2. X-ray diffraction (XRD)

X-ray diffractograms (XRD) was used for phase identification for the Al_xZr_{1-x} composites (figure 2). The Al₀Z₁₀₀ sample presented segregation of two crystalline ZrO₂ phases. First, well-resolved peaks matched well with the reflections of (110), (111), and (002) planes characteristic of monoclinic symmetry of ZrO₂ (*m*-ZrO₂; ICDD 24-1165) at 24.46, 31.48 and 34.18° in 2-theta, while the reflections of (111), (002), (220) and (311) planes located at 30.5, 35.2, 50.7 and 60.3° were associated with a metastable tetragonal phase of ZrO₂ (*t*-ZrO₂; ICDD 14-0534). However, the metastable tetragonal structure of ZrO₂ appeared at 1170 °C [33]. Opalinska *et al* [34] reported that the *m*-ZrO₂ phase. The crystallinity for the Al_xZr_{1-x} composites was calculated based on the ratio of the crystal area and the amorphous area as displayed by the XRD patterns, where the total integrated area of the XRD patterns is assumed to be an accumulation of background, amorphous and crystalline intensity in a selected from 10° - 60° . The relative crystallinity value contained an error of 12% as a result of sample preparation.

$$Crystallinity = \frac{A_{crystalline \ phase}}{A_{crystalline \ phase} + A_{amorphous \ phase}}$$

The crystallinity of the Al_0Zr_{100} sample was calculated and it previous equation, where presented a 60% of m-ZrO₂ phase dominance over 40% t-ZrO₂. In similar systems of Al_2O_3 -ZrO₂ it has been found that when the amount of Al_2O_3 is increased, the hardness increases, but the bending strength and fracture toughness decreased, owing to the effect of stress-induced transformation toughening of ZrO₂ became stronger. During the tetragonal-to-monoclinic transformation of ZrO₂, the bulk expanding took place [35].

On the other hand, the sample $Al_{100}Zr_0$ displayed two broad bands located at 45.90 and 67.09°, corresponding to reflections of (400) and (440) planes of cubic symmetry characteristic of Al_2O_3 (γ - Al_2O_3 ; according with Dabbagh *et al* [36] and ICDD 10-0425). The low resolution of the diffraction bands for the



Al₁₀₀Zr₀ sample was characteristic of relatively poorly crystallized of γ -Al₂O₃. For mixed oxides materials (Al_xZr_{1-x} with x = 25, 50 and 75), a drastic widening and intensity decrease of the peaks were observed, related to crystalline structures of ZrO₂ as the percentage of Al₂O₃ increased. This indicated a gradual reduction in crystallinity of these materials due to the incorporation of Al₂O₃. In this case, the decrease in crystallization during condensation reaction of alkoxides precursors forming mixed oxides [37]. The grain boundary structure of alumina influenced the resistivity of the material. One factor determining was the dislocations of aluminium atoms, these defects of dislocation and spinel formation are related with the tetragonal sites and an aluminium center has one electron trapped at an oxygen vacancy. This generates oxygen sites within the spinel-like block [38]. The coexistence of ZrO₂ and Al₂O₃ oxides were probably generated by a switch between zirconium cations and oxygen vacancies generated inside the composite.

3.2. Structural properties

3.2.1. ²⁷Al magic angle spinning nuclear magnetic resonance

The structural analysis for Al_xZr_{1-x} composites was acquired from the Magic Angle Nuclear Magnetic Resonance equipment for ²⁷Al, which exhibited information about aluminum environments for distinct aluminum peak positions. Aluminum is a quadrupolar nucleus with the chemical shifts for tetrahedral, pentahedral and octahedral species of aluminum with chemical displacement at ~60 ppm, 29 ppm and 0 ppm, respectively. This result was derived from exceptionally nonspherical coordination environments. The spectra are given in figure 3 for the Al_0Zr_{100} and $Al_{100}Zr_0$ samples and $Al_{25}Zr_{75}$, $Al_{50}Zr_{50}$ and $Al_{75}Zr_{25}$ composites with AlO_4 , AlO_5 and AlO_6 tags corresponding to three aluminum detectable species.

The Al₀Zr₁₀₀ sample presented no signal. Moreover, Al₂₅Zr₇₅ composite exhibited a weak signal for AlO₅ species indicating that low Al₂O₃ amount was not affecting the structure of the polyhedra coordination of the AlO₅ sites in this material was unusually distorted, similar to that in the case of crystalline Al₂SiO₅ polymorphs with oxygen type of Si-O-Al^V [39]. In our case a possible oxygen type can generate Zr-O-Al for AlO₅ species due to an homogeneous distribution inside the composite. Besides, the ratio integration of AlO₄ and AlO₆ species was approximately 1:6 indicating a blocking of AlO₅ sites. It was resonance corresponds to species with small quadrupolar interaction according to Wang *et al* [40], they associated an increase of the proportion of metastable AlO₅ to a more random distribution of metallic cations, related with higher homogeneity through aluminum nucleus surrounded by atoms which can produce an electron density larger. Additionally, Chen *et al* [41] correlate pentahedral aluminum to electron deficient sites, taking Lewis type acidity, acidity characteristic of γ -Al₂O₃ phase.

Nevertheless, $Al_{50}Zr_{50}$ and $Al_{75}Zr_{25}$ composites and $Al_{100}Zr_0$ sample showed an increase of AlO₆ species, associated with a replacement of oxygen in the lattice in octahedral symmetry, that possibly occurs by oxygen defects into the aluminum core. The AlO₆ groups building blocks for an O atom that was interlinking in three tetrahedral vacancies named 'oxygen tricluster' [42]. The increasing Al_2O_3 amount into Al_xZr_{1-x} composites generate presence of AlO₄, AlO₅ and AlO₆ sites showed strong evidence that a surface rearrangement has taken place. This behaviour suggested alternative charge compensation in the mechanism of networking modifiers for aluminium nucleus. We summarized in table 2, the area normalized for each Al species, where the AlO₄ and

Table 2. ${}^{27}Al$ MAS-NMR species relative amounts of the Al₂O₃-ZrO₂ composites.

Composite	$AlO_4(\%)$	$AlO_5(\%)$	AlO ₆ (%)	
Al ₀ Zr ₁₀₀	0.0	0.0	0.0	
Al ₂₅ Zr ₇₅	12.2	7.2	80.7	
Al ₅₀ Zr ₅₀	8.7	18.1	73.2	
$Al_{75}Zr_{25}$	5.7	26.4	67.9	
$\mathrm{Al}_{100}\mathrm{Zr}_0$	8.6	28.5	63.0	

AlO₆ species percentage area showed higher values for Al₂₅Zr₇₅ and Al₅₀Zr₅₀ composites than Al₇₅Zr₂₅ composite. This behaviour was associated for with concentration the free O²⁻ ions species where the coordinate modifier cations can form the Al-O-Al bonds which are modifiers of clustering by tricluster of Aluminium. However, AlO₅ species given a maximum local behaviour for Al₇₅Zr₂₅ composite associated probably owing to the removal of structural hydroxyls [43] retained into the Al_xZr_{1-x} network composite. Moreover, the AlO₄/AlO₆ ratio increases for Al₅₀Zr₅₀ composite, which means a blockage of AlO₅ species. The poor AlO₅ environment was detected for low Al₂O₃ content into Al_xZr_{1-x} composites, this effect promotes an electrostatic bond strength between oxygen and aluminum associated with donor ligands and poor cross-linking. The low Al-O-Al bond due to the stronger shielding around the aluminum center where the oxygen-donor ligands related with effects of Al₂O₃ doping are also relevant due to the variation of three types of the aluminum environment [44].

The environment for Al_xZr_{1-x} composites influenced by different Al₂O₃ amount was carried out through an ²⁷Al shift and narrow FWHM, the low intensities for AlO₄, AlO₅ and AlO₆ species presented behaviour distorted aluminium, this behaviour is given for sites where symmetry causing quadrupolar broadening and representing a masked signal. The AlO₄ species was bonded to the structural disorder and associated with oxygen vacancies due to higher surface oxygen available. These different factors occurring upon Zr⁴⁺ cations within the Al₂O₃-ZrO₂ network, which it can interact with pentahedral or octahedral sites with smaller electron density, the change in atomic structure is possibly due to a partially substituting Al³⁺ ion forming a new atomic arrangement caused by the binding energy and oxygen vacancies available modified the final electronic structure of Al_xZr_{1-x} composites.

3.2.2. X-ray photoelectron spectroscopy

The structural analysis of Al_xZr_{1-x} composites synthesized by sol-gel with different Al₂O₃ amount, was tested by X-ray photoelectron spectroscopy. Figures 4(a)–(f) presents XPS spectra of high-resolution of *O* 1s for (a) γ -Al₂O₃ reference, (b) Al₀Zr₁₀₀, (c) Al₂₅Zr₇₅, (d) Al₅₀Zr₅₀, (e) Al₇₅Zr₂₅ and (f) Al₁₀₀Zr₀ composites. The deconvolution analysis of *O* 1s core for Al₀Zr₁₀₀ and Al₂₅Zr₇₅ composites was resolved into two distinguishable peaks centered at ~532.00/530.11 and 531.55/529.82 eV respectively. The first peak corresponding with a satellite, this is due to core electron of oxygen is removed by a photoionization and the electron interaction with the valence electrons were exited (shake-up). Besides, the other peak corresponding to lattice oxygen corresponding with the oxygen superficial available [45].

Al₅₀Zr₅₀ composite showed 4 peaks at 532.93, 531.55, 531.44, and 529.82 eV, respectively. The first peak was associated with Al-OH bond on Al_xZr_{1-x} composite, possibly derived from hydroxides precursor of Al₂O₃. The second peak associated with ZrAl-O bond is related with the lattice and non-lattice oxygen ratio $(O_{non-lattice}/O_{lattice} \sim 1)$ for this composite was almost similar, it could be linked with the vacancies on surface and vacancies of bulk or insider are similar which we can assume the oxygen no vacancy will react with the reticular aluminum atoms and it can form an AlO_X interface layer lattice during the synthesis of the Al_xZr_{1-x} composite as already reported in the literature [46]. The third peak possibly is derived from ionizations of weakly adsorbed species and also ionizations of oxygen ions with particular coordination more specifically integrated in the subsurface (bulk structure near the surface). Finally, the fourth peak is associated with lattice oxygen. The non-lattice oxygen peak for all composites were low except for $Al_{50}Zr_{50}$ composite, where the ratio between both peaks was similar, which can be related with the increase in particle size and oxygen vacancy generated for the removal of interatomic hydroxyl groups. Composite Al75Zr25 showed a shift towards regions of higher energy for non-lattice and lattice oxygen than other composites figure 4(e). The shift in the position of the peaks have several explanations as follows: (1) the core level shifts are characteristically different because aluminum and zirconium cohesive energies are widely different (2) this change is directly related to the state of oxidation of the element where a high state of oxidation is related to a greater change in the binding energy, (3) share the element with its neighboring atom that was applied to the crystalline field generating asymmetry in the disposition of the bond and, (4) the shift generated made additional pressure to the element so that the binding energy required for



the expulsion of the electron is higher. In our case all composites spectra were calibrated respect to the *C*1*s* peak position at 285.00 eV binding energy where the interface layer is expected to be more stable and uniform than $Al_{100}Zr_0$ composite, allowing the generation of more stables composites.

Figure 5(a-d) presents XPS spectra of high resolution of Al2p for (a) $Al_{25}Zr_{75}$, (b) $Al_{50}Zr_{50}$,(c) $Al_{75}Zr_{25}$ and (d) $Al_{100}Zr_0$, respectively. For $Al_{25}Zr_{75}$ and $Al_{75}Zr_{25}$ composites the Al2p spectra showed two shoulder, at 74.80 and 73.42 eV binding energy related with Al2p and with changes in elapsed time [47] where the $Al2p_{1/2}$ peak was higher than $Al2p_{3/2}$ peak related with an oxide character of the composite. $Al_{50}Zr_{50}$ composite presented three peaks associated with Al-OH, ZrAl-O and Al_2O_3 : ZrO_2 with center at 74.80, and 73.42 eV, respectively. The shift of the first peak is related with binding Al-OH inner surface and the ZrAl-O bond into Al_xZr_{1-x} composite is due to metal character.

Argon modified the oxides species during XPS analysis on the superficial composites, this effect of the apparent enrichment of Al³⁺ oxidized forms a mixed oxide Al₂O₃:ZrO₂ into the composites observed by the *Al* 2*p* peaks. Also, the FWHM was wider than other composites related to restructuring an increment of particle size. The mixed Al₂O₃:ZrO₂ composite dominant character associated with a good hydroxyl groups elimination from condensation reaction during the composites synthesis.

Finally, the Al₁₀₀Zr₀ composite only presented γ -Al₂O₃ phase from XRD analysis derived from sol-gel synthesis where the gradual dehydroxylated from hydroxyls such as boehmite (AlO(OH)) and water molecule [48].

The preservation phase is linked to the conformation of electron neutrality during the synthesis, some cationic defects must therefore be created in the structure due to the hydroxyl removal and obtain a number of vacancies with difference of geometries. The conformation of Al_2O_3 - ZrO_2 had vacancies produced by poor hydroxyl groups associated with octahedral symmetry previously founded with ²⁷Al MAS-NMR results, and according with Sen *et al* [39].

Additionally, the high resolution of XPS spectra of Zr 3d peaks for (a) Al_0Zr_{100} , (b) $Al_{25}Zr_{75}$, (c) $Al_{50}Zr_{50}$ and (d) $Al_{75}Zr_{25}$ composites are shown in figures 6(a)–(d), respectively. Based on the results, the Zr 3d peaks are subject to a chemical shift of about 4 eV in $Zr0_2$ relative to the metal character. Moreover, the spin–orbit splitting of the Zr 3d core levels is 2.3 eV so that the XPS spectrum consists of two well-resolved shoulders [49]. The two shoulders observed $Zr 3d_{3/2}$ and $Zr 3d_{5/2}$ peaks at ~183.755 and 181.45 eV, respectively, in agree with previous



works [50, 51]. There was a slight change in the BE of the Zr 3d peaks with an increase of Al₂O₃ amount related to some zirconium atoms fail to enter into the Al₂O₃ lattice. The composites with NH₄OH have been affected during the process of synthesis due to an active restructuration, where the $Zr 3d_{3/2}$ and $Zr 3d_{5/2}$ with a 2.27 eV spin—orbit presented 1:3 ratio of height. The effect of Al₂O₃ amount into composite in each curve line shapes are not changed during the measurements and they do not exhibit impurities or small amounts of oxidation to higher binding energy, the asymmetric peak shape observed is agreement with Juma *et al* [52], zirconium oxides are not electronic but ionic conductor from removal of electrostatic charges by XPS equipment, hence an increase of particle size shift to higher binding energies. The results obtained of deconvolution analysis of the Zr $3d_{5/2}$ and $Zr 3d_{3/2}$ spectra, showed 56.5% of total area for $Zr 3d_{5/2}$ and decrease at 37.3% after deconvolution analysis for Al₅₀Zr₅₀ composite. For this composite the formation of Al₂O₃:ZrO₂ mixed composited was related to more O lattice amount than other composites.

The influence of Al_2O_3 on Al_2O_3 - ZrO_2 composites is emphasized in the following paragraphs. As can be noted from table 3 presents XPS binding energies (eV), the peak position of the Al2p and for $Al_{50}Zr_{50}$ composite shifted to higher BE with Al-OH, ZrAl-O and the mixed Al_2O_3 : ZrO_2 composite at 76.41, 74.80, and 73.42 eV. These shift to higher BE indicates an increasing amount of Zr in substitutional sites of Al_2O_3 because of the higher electronegativity of Al (1.5) compared to Zr (1.4). Additionally, the FWHM are wider than all composites, it was possibly related to a rough surface and chemical interaction between oxides mixed with high particle size, the oxygen attached to different atoms (Al or Zr) shifts due to the difference in shielding effect.

The non-lattice and lattice oxygen ratio, decrease as a function of Al_2O_3 amount, suggesting that the superficial oxygen available is higher than the bulk oxygen, which can act as a source or a sink for oxygen for $Al_{50}Zr_{50}$ composite was low possibly associated with oxide character predominance.

3.3. Morphological structure

3.3.1. Scanning electron microscopy (SEM)

Figure 7 shows the SEM micrographs of the Al_xZr_{1-x} composites for (a)-(b) $Al_{25}Zr_{75}$, (c)-(d) $Al_{50}Zr_{50}$ and (e)-(f) $Al_{75}Zr_{25}$ with 15000 x and 30000 x of magnification, respectively. In general, all presented irregular aggregates, the method of preparation showed morphology similar to coral shape due to the sintering phenomenon due to stacking and agglomeration effect along the composites. The micrographs show an increase in particle size



respect the Al_0Zr_{100} sample in the same way that Sherafat *et al* [53], It is worth mentioning that they founded 15 and 27 nm of particle size corresponding *t*- and *m*-ZrO₂ phases, prepared without stabilizing additives by slow alkaline precipitation, the particle sizes were determined by specific BET surface-area measurements.

The restructuration of Al_xZr_{1-x} composite was observable used NH₄OH as additive of synthesis, and Al₂O₃ amount effect, which produced agglomeration of particles of the different sizes from the condensation reactions between metal-organic precursors, during the reaction both lost a molecule of water. The morphological properties by both effects showed no crack along the grain frontier and a small increase in grain size of the composites. The total porosity depends to a large extend homogeneity and the phase distribution inside the composite. The pressure and temperature can modify the porosity due a rearrangement of the Al₂O₃-ZrO₂ cluster, in this case the Al₂O₃ can modified de porosity due the pores are interconnected three-dimensionally in the porous with different cations ratio generating pores compacts. The high porosity of composites is due to the chain growth mechanism directly related to the middles of the polymeric chains rather than to the ends promotes lower surface energy [54].

3.3.2. High angle annular dark field or Z-contrast (HAADF)

Z-constrat images is type of backscattered electron were incident electrons back from a target specimen and imaged with scanning electron microscope. The atomic number or composition determines an image contrast, orientation of the crystal structure which determines the contrast image. Al_xZr_{1-x} composites images are shown in figures 8(a)–(c) for $Al_{25}Zr_{75}$, $Al_{50}Zr_{50}$ and $Al_{75}Zr_{25}$ composites, respectively. The images showed the density of atomic number, in which the Zr^{4+} ion diffracted secondary electrons with higher intensity (brighter), the different orientation of ZrO_2 into the network of Al_xZr_{1-x} composites was observed.

 $Al_{25}Zr_{75}$ composite showed ZrO_2 grain with high bright in *Z*-contrast image in concordance with Suenaga et al [55]. These composites seem to be segregated between Al_2O_3 and ZrO_2 , where Al_2O_3 coats rods of ZrO_2 with a length at ~250 nm. The single nanocrystals of monoclinic or tetragonal zirconia phases well-dispersed inside the matrix of Al_2O_3 . $Al_{50}Zr_{50}$ composite presented faceted morphology where the Al atoms were randomly integrated into the zirconia lattice as a substitutional solid solution obtained segregation phases by additive of synthesis and Al_2O_3 amount effects. The substitution of some Al by Zr atoms in the monoclinic or tetragonal

	O 1s		Zr3d		Al2p	
			(eV)			
Composite (<i>Chemical</i> %)	ZrO ₂ Al ₂ O ₃	Al ₂ O ₃ :ZrO ₂	ZrO ₂ 3d _{5/2} 3d _{3/2}	Al ₂ O ₃ -ZrO ₂ 3d _{5/2} 3d _{3/2}	Al ₂ O ₃	Al ₂ O ₃ :ZrO ₂
Al ₀ Zr ₁₀₀	530.1		181.45			
	1		(56.5)			
	(83.7)		183.75			
	532.0 0 ^a		(43.5)			
	(16.3)					
Al ₂₅ Zr ₇₅	529.8	531.55	181.67		73.42	74.80
	2	(9.6)	(56.5)		(83.6)	(16.4)
	(90.4)		183.98			
			(43.5)			
$Al_{50}Zr_{50}$	529.8	531.44	181.67	183.63	73.42	74.80
	2	(23.2)	(37.3)	(19.9)	(42.7)	(37.1)
	(52.6)	532.93ª	183.98	185.93		
	531.5 5 ^a	(3.9)	(27.9)	(14.9)		
	(6.8)					
$Al_{75}Zr_{25}$	529.8	531.40	181.67	183.67	73.42	74.80
	2	(27.2)	(50.0)	(7.6)	(65.8)	(34.2)
	(61.7)	532.93ª	183.98	185.93		
	531.5 5 ^a	(4.9)	(38.1)	(4.4)		
A1 7.	(0.2)				73 50	
$M_{100} \Sigma I_0$	(100)				/ 5.50	
	(100)			(100)		

Table 3. XPS binding energies of O 1s, Zr 3d, and Al 2p core level and chemical percent of the Al_2O_3 - ZrO_2 composites.

^a Satellite (shake-up).

Other contributions: $Al_{50}Zr_{50}$ content 20.2% of Al-OH with core levels *O 1s* (533.15 eV) content 13.5% and *Al2p* (76.41 eV).

zirconia lattice was directly observed by HAADF-STEM analysis. Finally, $Al_{75}Zr_{25}$ presented homogeneous distribution of aluminum and zirconium, where the aluminum atomic sites of the boundary core regions are consistent with the O-terminated grain boundary structure model, the slight intensity in this composite presented fluctuations were founded in the experimental images, which may be related to local structural variability and vacancies in the grain boundary [56].

Finally, based on experimental results above presented and early reports [57, 58]. We proposed a possible configuration of Al_xZr_{1-x} composites as a function of Al_2O_3 is shown in figure 9. Low Al_2O_3 content changed the configuration of Al_xZr_{1-x} composites seems to be affected by the addition of Al-OH where the formation of oxygen vacancies is blocked by high consumption of oxygen due to tetrahedral and octahedral species of aluminum domain which presented oxide character where the proper cation distribution generated a restructuration with grain size moderate and crystal with random distribution.

Nevertheless, high level of aluminum content on Al_xZr_{1-x} composites showed pentahedral Al species of aluminum associated with homogenous cations distribution, besides non-lattice and lattice oxygen amounts were similarly related to the same oxygen vacancies in the bulk and superficial. At the same time the Al-OH and AlZr-O bonded are observable related with the coexisted of metal and oxide character. The Al₂O₃:ZrO₂ mixed was due by cations mobility in bulk and superficial which improvement textural, structural and morphological properties of Al_xZr_{1-x} composites.

4. Conclusions

The sol-gel method was used to synthesize Al_2O_3 - ZrO_2 composites and led to the formation of solid solutions upon calcining at 773K for 5h. The additive of synthesis and Al_2O_3 amount provide changes into adsorption-desorption isotherms associated with different pore type all inside the range of mesoporous materials. The X-ray



Figure 7. SEM micrographs of Al_2O_3 - ZrO_2 composites for (a)-(b) $Al_{25}Zr_{75}$, (c)–(d) $Al_{50}Zr_{50}$ and (e)–(f) $Al_{75}Zr_{25}$ with 15000 x and 30000 x of magnification, respectively.

diffraction patterns presented micro crystallinity and a new mixed phase in close interaction with each other. The Al_xZr_{1-x} composites would allow a greater critical inclusion grain generated high surface areas and therefore a more stable system regarding the transformation of zirconia phases, not only stabilized the tetragonal phase also leads to the generation of oxygen vacancies in the Al_xZr_{1-x} composites.

Particularly, the textural, structural and morphological analysis generate important changes, especially for $Al_{50}Zr_{50}$ composite with higher surface area, and pore volumes, also the AlO_4/AlO_6 ratio of aluminum species was high possibly related with the octahedral chains are crosslinked by double chains of $(Al-Zr)O_4$ in tetrahedral species and the substitution of Zr by Al produces O vacancies in the formation of tetrahedral clusters. The porosity and particle size were improvement for this composition, which is related with higher values of oxygen lattice than non-lattice promoting an oxygen superficial, and non-lattice oxygen related with available oxygen in the bulk, this behaviour improve the electronic structure. Also the last one can be related with adsorbed oxygen on the particle surface due to the mesoporous structure. When increasing the aluminum amount in the





composites the upper value of the valence band of Al₂O₃ is greater and is formed by the non-bonding O $2p_{\pi}$ orbitals associated with the presence of large masses with effective holes derived from the vacancies generated by the Zr atoms. Finally, the SEM micrographs and *Z*-contrast showed a modulated morphology and porosity as a function of Al₂O₃, we founded the optimal composition of Al₂O₃ into Al_2Zr_{1-x} composites with a homogeneous dispersion of the components as well as understanding the interface between Al₂O₃ and ZrO₂ responsible for their physical-chemical properties.

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