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Revealing the effects of high Al loading incorporation in the SBA-15 silica mesoporous material

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Abstract

High aluminum loading incorporation in the SBA-15 silica structure was investigated. Different Si/Al molar ratios (15, 10, and 2) were evaluated. The SBA-15 and the aluminum-containing materials (Al-SBA-15) were prepared by the “pH adjusting” method with modifications. The mesoporous structure of the materials was demonstrated by the type IV isotherms. The SBA-15 pore changed from a cylindrical to a slit-like structure in the presence of higher aluminum content. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) pointed out that the structural order is compromised in the presence of a higher aluminum load in the Al-SBA-15 materials, although the mesoporous structure was preserved. Higher Al loading increases the total quantity of Lewis acid sites as well as generates Brønsted acid sites. CO adsorption FTIR spectroscopy suggests aluminum incorporation into the SBA-15 and generation of acid sites. The Si-O-Al linkage in the aluminum-containing materials was corroborated by UV-Vis DRS due to the presence of a peak centered at 241 nm related to the Al-O bond, which is ascribed to four-coordinated framework aluminum in the SBA-15 structure. XPS spectra of Al 2p suggested that the Al species are less oxidized than the Al₂O₃ phase giving some indication of Al incorporation into the SBA-15 framework. ²⁷Al MAS NMR results revealed that the aluminum species are in a tetrahedral oxygen coordination environment for Al-SBA-15 with Si/Al molar ratios of 15 and 10. Aluminum species in both tetrahedral and octahedral environments were evidenced for Al-SBA-15 with a Si/Al molar ratio of 2.

Keywords: *SBA-15; aluminum-incorporation; mesoporous; textural; structure; acidity*

Highlights

- SBA-15 and Al-SBA-15 were synthesized by the “pH adjusting” method.
- Textural, structural, acid, and surface properties differ with the Si/Al ratio.
- Spectroscopic results point to the incorporation of Al into the SBA-15 framework.
- Extra-framework Al species were formed in the Al-SBA-15 with the highest Al load.

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1. Introduction

The development of advanced materials has acquired an important place in researched applications in recent times following the quest to provide significant advances in energy uses and other matters such as contaminant removal, drug release, bio-sensing, membrane separation, adsorption, and separation, including the field of catalysis [1]. In this sense, due to the remarkable properties offered by mesostructured siliceous materials e.g., well-defined pore architecture, a high surface-to-volume ratio, and the ability to incorporate other heteroatoms into their mesostructure, they have been consolidated as one of the most attractive materials for multiple applications. This is since, in distinction to most conventional solids (crystalline or amorphous), mesostructured silica materials consist of mesoporous channel systems that give rise to new opportunities in the field of materials chemistry [2].

After the discovery of MCM-41 and the concomitant development of the M41S family, special efforts have been focused on the development of mesoporous solids based on the supramolecular templating approach (surfactant-templated materials) due to the versatility, simplicity, and robustness involved in their synthesis methodology and to the ability to generate systems with very complex and interconnected porous structures [3-5]. Within this class of materials, mesoporous silicas, SBA-15 has received special consideration due to its improved structural stability compared to its counterparts belonging to the M41S family that has a similar mesopore organization [2, 6, 7]. The SBA-15 exhibits a large pore size and thicker pore walls which provides it with greater thermal, mechanical, and chemical resistance. In addition, its uniformly distributed mesopore matrix improves accessibility for substrate diffusion and adsorption, making them one of the auspicious materials for potential applications. Now all these features that SBA-15 exhibits are the result of the strategic combination of the fundamentals of sol-gel chemistry and template synthesis, and they can be modulated and controlled through the variation of the parameters involved during the synthesis process. A common synthesis requires a non-ionic triblock copolymer as a structure-directing agent, typically Pluronic P123 that consists of hydrophilic polyethylene oxide (PEO) units and hydrophobic polypropylene oxide (PPO) units and a silica source which can be tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS) or tetrapropyl orthosilicate (TPOS). The formation of the hexagonal arrangement and uniform mesoporous channels occurs through a mechanism of interaction between the hydrolyzed silica species with the surfactant or template interface in strongly acidic media. This process is described by the solubilization of the tri-block copolymer by association with hydronium ions (H_3O^+) with the hydrophilic units PEO of the surfactant and the hydrolysis of the silica precursor to give rise to the formation of cationic silica species followed by their partial oligomerization of these with the already hydrolyzed PEO units of the surfactant through electrostatic and Van der Waals interactions. This leads to the formation of organic-inorganic hybrid

micelles that gradually organize in the form of a honeycomb and generate the tubular structure [8]. However, despite its qualities of structural uniformity, size, order, and uniform distribution of its pores, all of which are often not sufficient to satisfy certain application requirements, particularly due to their inert character because of its overall neutral framework and the absence of active components. Hence, the functionalization of SBA-15 through the incorporation of heteroatoms in its structure becomes much more indispensable to exceed certain limitations. Its functionalization capacity allows the opportunity to optimize this kind of system by insertion of metal ions or heteroatoms into the neutral silica framework and thus achieve materials with diverse acid-base or redox properties for multiple scientific and technological applications [2, 3, 9, 10].

From the available literature, various studies have described the incorporation of heteroatoms such as Al [11-13], Ga [14], Fe [15], Zr [16], Ti [17, 18], or Nb [19] to name a few, with the aim of tuning and improving either the acid-base or redox properties of SBA-15. Various studies have demonstrated that the incorporation of Al into the siliceous mesoporous network has been effective for the creation of acid sites in its use as an acidic solid catalyst or as a carrier material for the dispersion of metal nanoparticles (NPs) and also to improve their hydrothermal stability [13, 20-22]. It has been reported that the coordination environment of the aluminum species influences the nature and strength of the acid sites that these species can provide to SBA-15 due to a linear relationship between the ratio of Brönsted/Lewis acid sites (C_B/C_L) and the proportion of tetrahedral species [12]. Nevertheless, the incorporation of aluminum into the mesoporous silica is not straightforward requiring fine control of the synthesis procedures as explained in more detail as follows [13, 23]. Normally the synthesis of SBA-15 is carried out in acidic medium ($\text{pH} \sim 1$) in order to precipitate silica (isoelectric point, $\text{IEP} \sim 2$), increase the cationic charge density of the medium, and thus promote cooperative self-assembly of the silicon ions with the pre-formed template structure, conducted by hydrolysis and condensation reactions giving rise to the hybrid organic-inorganic interface and consequently the formation of the hexagonal mesophase of SBA-15 [2]. This pH condition of the medium has a relevant aspect on the solubility of the Al precursor, since at $\text{pH} \sim 1$ the aluminum is only present in its cationic form (Al^{3+}), preventing its condensation on silicon species to generate Si-O-Al bonds due to electrostatic repulsion between the Al^{3+} ions and the silica species which suppresses the favorable contact between them [24, 25]. Then, since in these acidic hydrothermal conditions the dissociation of Al-O-Si bonds is promoted and the difference between the hydrolysis rates of silica and aluminum is usually very high, the insertion of Al into the mesostructure results less efficient.

Several methods or synthetic strategies to introduce the Al species in the SBA-15 have been adopted to overcome these circumstances. Among the most common preparation strategies reported it is included direct synthesis [23, 26, 27], post-synthesis [22, 28, 29] and “pH adjusting” [24, 25, 30]. The post-synthesis routes

could lead to the formation of large amounts of Brönsted and Lewis acid sites; however, it has the disadvantage that during the filtration process, most of the Al can be removed during washing, since the Al is incorporated by immersion of the SBA-15 solid into the gel. In addition, they are relatively complex, involving many steps with the use of organic solvents, inorganic salts, and stringent conditions requiring the absence of water and oxygen, which makes them less feasible because of the extensive and environmentally unfriendly process involved [25, 27, 31, 32].

The direct synthesis approach is much simpler, where the aluminum precursor is added directly to the synthesis gel, avoiding additional processing steps which result in a decrease in the final cost of the material preparation [33, 34]. Nevertheless, often the Al species are not retained in the silica network and are condensed to polymeric species which results in extra-framework locations. For example, Lin et al. [27] reported the incorporation of Al into the lattice of SBA-15 by acid-free hydrothermal treatment in two days. However, the molar ratios of the final products are difficult to control in a pH range between 3.1 and 3.5, managing to introduce up to 42% mol of the initial gel composition because of the easy dissociation of Al-O-Si bonds. Also, a direct Al-SBA-15 synthesis providing a high yield of tetrahedral Al (Al_{Td}) has been demonstrated, using the one-pot method with various organic aluminum salts [33, 35, 36], such as aluminum acetate, aluminum citrate, aluminum acetylacetonate, and aluminum isopropoxide. But the one-pot method is not applicable with inorganic aluminum salts because in more basic conditions the incorporation of Al is not efficient either, due to its greater tendency to form $\text{Al}(\text{OH})_3$ and the precipitation of silica is unlikely because its isoelectric point is equal to $\text{pH} = 2$. In another study, the direct synthesis method has been reported with low pH values, providing materials with high specific surface area and pore volume, however again, only a limited amount of Al from the initial gel synthesis is incorporated in the final solid because a high amount of aluminum is present outside the network as a result to the low pH value of synthesis [24].

In view of the drawbacks presented by the direct synthesis and post-synthesis methods in terms of low Al incorporation from the synthesis gel to the final solid, the two-step pH adjusting method has been developed to achieve a better insertion of heteroatoms such as Al into the walls of ordered mesoporous silica materials under these strongly acidic medium conditions. In the “pH-adjusting” method the heteroatom source is added to the initial reaction mixture in strongly acidic media ($\text{pH} \sim 0$). When the hexagonal mesophase is formed, the pH value of the system is adjusted to neutral pH of 7.5, followed by a hydrothermal treatment for another period of time, during which a large amount of heteroatoms can be introduced into the mesophase [24, 30]. Hence, by the “pH adjusting” step, random incorporation of Al into the structure of SBA-15 is minimized and considerable differences between the Si/Al ratios of the initial gel and the final product are avoided. It should be noted that aspects such as the synthesis approach as well as the selection

of the variables of reaction involved such as the nature of the Si and Al precursors used [11, 37-42], the type of acids used as media [34, 43-45], the control of the H₂O/HCl molar ratio [11, 26], the temperature and time of the synthesis of initial gel mixture [45-47], among others [26, 48, 49] can influence the physicochemical properties and the quality of the final material. Moreover, according to Vasconcelos et al. [50], the order in which the Si and Al precursors are added in the hydrothermal synthesis (simultaneously, separately, or in intervals) affects the characteristics of the material. The results of this study indicated that the addition of the Si precursor first and then the Al, with a pre-hydrolysis pause between them, generates materials with better properties. Besides, previous studies [46-48] have shown that an increase in the gelation temperature to 60 °C allows the development of more ordered mesopores of the mesophase-precursor because at lower assembly temperatures it does not lead to a proper stretching of the template, while at higher temperatures the rupture of the molecular template occurs. Studies [45, 46] have also indicated that the assembly of the silicate with the surfactant occurs rapidly during the first 2 h of gelation. Considering the need to optimize preparation times, the latter allows for minimizing the synthesis period which is desirable in practical terms.

In short, great efforts have been pushed to obtain mesoporous aluminosilicates with high Al content that show high acidity without considerably affecting their structural order and morphology or increasing the complexity of the synthesis. A method that allows the stoichiometric incorporation of Al is not yet feasible [39] and despite the potential and novelty of the “pH adjusting” approach in the incorporation of large amounts of heteroatoms, the optimization of the parameters of this method is still an open research topic. Thus, a better understanding of the acidic, strength of acid sites, textural, structural, and surface properties of the mesoporous aluminosilicates is strongly required to enable their efficient design and application of silica mesoporous material with high loading incorporation of Al heteroatom.

Aluminum is considered the most appropriate element to be inserted into the silicon framework of the SBA-15 due to its similar properties and atomic size referred to the silicon element. In addition, it has proven to be a very valuable alternative for the generation of surface acid sites by its characteristics of small size and high charge density [48]. As mentioned above, the functionality promoted by the introduction of Al into SBA-15 has resulted in an advantageous mesoporous material with catalytic applications, either properly used as an acid catalyst or as a material for the incorporation of an additional catalytic phase [12, 51, 52]. Considering part of this background exposed regarding the adjustment of the synthesis parameters, the incorporation of high aluminum loading in the SBA-15 structure was studied in this work.

Different Si/Al molar ratios were evaluated and the role of high aluminum loading incorporation in the texture, structure, acidity, and surface properties of SBA-15 was explored. This work was devoted in the

elucidation of the effect of high aluminum loading in the pore shape, structure order, and the preservation of the hexagonal arrangement of the SBA-15. It was focused on the clarification of the presence of extra and intra-framework aluminum species and their interdependence with the Si/Al molar ratio. A substantial fraction of Al species to be introduced in tetrahedral coordination must be strongly dependent on the Si/Al molar ratio. Insights were pursued on the interaction of aluminum with silanol groups of the silica mesoporous matrix. Spectroscopic characterization was used to reveal the generation of acid sites due to the incorporation of high aluminum loading in the SBA-15. To our knowledge, this is the first time that such a deep characterization is reported for this type of material, despite the large number of reports concerning the incorporation of heteroatoms into these mesoporous structures. Here we show insights into the incorporation and location of Al atoms in the structure as a function of aluminum loading (which is particularly high) and how this affects the material characteristics.

2. Experimental

2.1 Synthesis of SBA-15 and Al-SBA-15

Mesoporous silica SBA-15 containing aluminum was prepared according to the “pH-adjusting” method reported by Wu et al. [30] with modifications. The difference from the procedure described by Wu et al. is that $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, Sigma-Aldrich, USA) was used as the aluminum source instead of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$; as well as the adoption of a shorter reaction time of gel formation (the suspension was stirred during 2 h after the addition of TEOS instead of 4 h and the second gelation step after the addition of Al-precursor was shortened to 2 h instead of 20 h). Also, the temperature at which the mixture was stirred during the first stages of the synthesis was 60 °C instead of 40 °C and the pH of the reaction mixture was adjusted by adding a potassium hydroxide solution (5 M KOH). Pluronic P123 (5800 g mol⁻¹, EO₂₀PO₇₀EO₂₀, Sigma-Aldrich, USA) was used as the template, and tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich, USA) as the silica source. In a typical synthesis, 12.0 mL of concentrated HCl (37 wt.%, Merck) solution was added in 100 mL of water. 4.0 g of Pluronic P123 was dissolved to the prior solution at 60 °C and this suspension was vigorously stirred in a closed flask for 2 h, during which time the suspension was homogeneously cleaved. Then 8.55 g of TEOS was added dropwise (pre-hydrolysis source) and stirred for another 2 h. Next, aqueous solutions of different concentrations of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added for the desired Si/Al ratio (Si/Al = 15, 10, 2) to get in the initial gel. This solution was added to the mixture of reaction and it was kept under magnetic stirring for 2 h. Subsequently, the mixture was hydrothermally treated in a glass reactor at 90 °C for 48 h. After the hydrothermal treatment, the pH of the mixture was adjusted to 7.50 with the dropwise addition of a 5 M KOH (Merck) solution and again the

system was hydrothermally treated in the same conditions. Finally, the formed solid was recovered by filtration, washed, dried at 100 °C for 2 h, and calcined to 500 °C for 5 h (2 °C·min⁻¹). These solid samples were labeled as SBA-15 Si/Al *x*, where *x* is the value of the nominal molar ratio Si/Al. In the case of the synthesis of pure SBA-15 (molar ratio Si/Al = ∞), it was prepared following the above procedure, except for the addition of the Al precursor in conjunction with the second hydrothermal treatment and pH adjustment and was labeled as SBA-15 (This is presented in Scheme 1 of the Supplementary Material). A new reference SBA-15 material was prepared following the same synthesis route used for the preparation of Al-SBA-15 materials. The details about the synthesis and its characterization are included in the Supplementary Material (Fig. S1, Fig. S2 and Table S1).

2.2 Characterization

The Shimadzu EDX-720 energy dispersive spectrometer was used to perform X-ray fluorescence analysis (XRF). The equipment has an X-ray tube with a rhodium (Rh) anode that operates between 5-50 kV and 1-1000 µA. This technique allows qualitative and quantitative analysis of elements with atomic weights between sodium (Na) and uranium (U) and was used to determine the real Si/Al molar ratio in the samples.

N₂ adsorption-desorption analyses at -196 °C were performed in a Tristar II series Micromeritics to evaluate the textural properties of the samples. The BET and BJH methods were used for the calculations of the specific surface area and porous properties (size distribution and volume) of the mesoporous SBA-15 aluminosilicates, respectively. Before the adsorption measurements, the samples (approximately 100 mg) were degassed at 120 °C for 2 h under a flow of N₂ to remove impurities retained on the surface.

X-ray diffraction measurements (XRD) were made using a Bruker-AXS D8-Advance diffractometer with vertical theta-theta goniometer, incident- and diffracted-beam Soller slits of 2.5°, a fixed 0.5° receiving slit and an automatic Air-scattering knife on the sample surface. The low 2θ range was between 0.5 and 10° by using the software option Variable Detector Opening with an angular step of 0.02° at a step/time of 1.0 s. The wide 2θ range was between 5 and 80° with an angular step of 0.02° at a step/time of 0.5 s. CuK_α radiation was obtained from a copper X-ray tube operated at 40 kV and 40 mA. Diffracted X-rays were detected with a PSD detector LynxEye-XE-T with an opening angle of 2.94°. Samples were deposited on a low-background (Si (510)) support. The profile analysis of the diffractograms was performed with the software TOPAS by considering a hexagonal cell [53] and refining only the *a* parameter and the peak width. Profile fitting [53] was performed with the TOPAS v6 software [54, 55]. The background was modeled with a 3rd order Chebyshev polynomial. The instrumental contribution to the diffraction profile was calculated with

the LaB₆ (NIST SRM 660c). The peak width of each phase was modeled with the Double-Voigt Approach [56] by considering only the Lorentzian contribution of the crystallite size effect and discarding any contribution of the microstrain to the peak width. The averaged integral breadth was obtained from the resulting fitted Voigt function to the whole diffractogram [57].

Temperature-programmed desorption of NH₃ (NH₃-TPD) experiments were carried out in a quartz cell using a Micromeritics Autochem II 2920 automatic equipment. Prior to the measurements, the sample (ca. 50 mg) was reduced at 400 °C (5 °C·min⁻¹) for 2 h in H₂ flow (20 mL·min⁻¹). After that, the system was cooled to 40 °C under Ar flow (20 mL·min⁻¹) and the gas was switched to NH₃ (20 mL·min⁻¹) for 10 min at 40 °C. Then, the sample was heated to 75 °C (5 °C·min⁻¹) under an Ar flow (20 mL·min⁻¹) to remove physically adsorbed (weakly held) NH₃. The total amount of desorbed ammonia in the samples was obtained by the standardized ammonia TPD peaks areas following the calibration of the thermal conductivity detector (TCD).

The morphology and elemental mapping of the materials were observed by high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy-dispersive X-ray (EDX) spectroscopy using an FEI Tecnai F20 microscope equipped with a field emission source with a point-to-point resolution of 0.19 nm and accelerating voltage of 200 kV. A small amount of sample was suspended in methanol, sonicated, and dispersed. Then a drop of the suspension was placed onto a microscope copper grid with a holey carbon film.

The *in-situ* Fourier Transform Infrared spectroscopy (FTIR) technique with adsorbed pyridine was used to determine the concentration of acidic sites (Brönsted and Lewis) of the materials using a transmission cell with CaF₂ windows in a Bruker spectrometer (Vertex 70) equipped with an MCT detector. The background was carried out at 150 °C under an Ar atmosphere (100 mL·min⁻¹) after 30 min of heating. For analysis, a 12 mm sample self-supporting pellet was pretreated at 350 °C under an Ar atmosphere (100 mL·min⁻¹) for 60 minutes. Then, the system was cooled to 150 °C and pyridine vapor was injected until the sample was completely saturated. The excess physically adsorbed pyridine was purged with Ar (100 mL·min⁻¹). FTIR spectra were collected at 150 °C with a resolution of 4 cm⁻¹ in the region of 4000 to 1200 cm⁻¹. The spectra of the samples without and with adsorbed pyridine were subtracted. The acid sites were quantified based on the Lambert-Beer equation:

$$A_i = \frac{\varepsilon_i W C_i}{S} \quad (\text{Eq. 1})$$

Where A_i (cm^{-1}), ε_i ($\text{cm} \cdot \mu\text{mol}^{-1}$), W (mg), C_i ($\text{mmol} \cdot \text{g}^{-1}$), and S (cm^2) are the integrated absorbance, integrated molar extinction coefficient, sample mass, the concentration of the i species, and sample disk area, respectively. The ε_i values for the pyridinium ions bonded to Brönsted acid sites and pyridine coordinated to Lewis acid sites were $\varepsilon_{B,Py}$ (1545 cm^{-1}) = $1.23 \text{ cm} \cdot \mu\text{mol}^{-1}$ and $\varepsilon_{L,Py}$ (1450 cm^{-1}) = $1.73 \text{ cm} \cdot \mu\text{mol}^{-1}$, respectively [58].

FTIR of adsorbed CO was performed on a Bruker Vertex 70 spectrometer equipped with an MCT detector operating at 4 cm^{-1} . The *in-situ* infrared cell used in the experiments was a $2\frac{3}{4}$ " stainless steel cube equipped with KBr IR windows. The cell was connected to a gas handling/pumping station and through both leak and gate valves to a quadrupole mass spectrometer (UTI 100C). The sample was pressed onto a fine tungsten mesh, which in turn, was mounted onto a copper sample holder assembly attached to ceramic feedthroughs of a 1.33" flange. The sample temperature was monitored through a chromel/alumel (K-type) thermocouple spot-welded to the top center of the tungsten mesh. Prior to the measurements, the sample was heated to $500 \text{ }^\circ\text{C}$ and kept on this temperature for 2 h to ensure the removal of all water from the material. The base pressure of the cell was less than 2×10^{-8} Torr. Finally, the sample was cooled down to $-193 \text{ }^\circ\text{C}$ for the CO adsorption measurements. Prior to each spectral series acquisition, a background spectrum was taken of the adsorbate-free (clean) sample. For each sample, the adsorption of CO was performed by gradually increasing the equilibration CO pressure in the cell to a final pressure of around 0.350 Torr. An FTIR spectrum of adsorbed CO was recorded after the introduction of each CO aliquot. After the FTIR measurements, each sample was annealed to $377 \text{ }^\circ\text{C}$ and finally cooled to RT.

Diffuse reflectance spectra (UV-Vis DRS) of the samples were recorded on a Thermo Scientific spectrometer (model Evolution 300) equipped with a Harrick diffuse reflection accessory (Praying Mantis) in the range of 200-1100 nm. The original data of the reflectance spectra (% R) as a function of wavelength (λ) were treated with the Kubelka-Munk function and the modified Kubelka-Munk function [59, 60] to determine the optical absorption edge energy values (E_b) as indicated by the following equations:

$$F(R_\infty) = \frac{(1 - R)^2}{2R_\infty} = \frac{\alpha}{S} \quad (\text{Eq. 2})$$

Where $F(R_\infty)$ corresponds to the reflectance transformed according to the Kubelka-Munk function, R is the reflectance of the sample and R_∞ the reflectance of the reference sample. This expression directly determines the relationship between the absorption (α) and scattering (S) coefficients and the reflectance ratio between the target sample and the reference sample, measured at an infinite penetration distance. Considering the energy-independent scattering coefficient, the Kubelka-Munk function can be assumed proportional to the absorption coefficient which is defined by the following expression:

$$\alpha = \frac{(h\nu - E_b)^\eta}{h\nu} \quad (\text{Eq. 3})$$

and thereby the modified Kubelka-Munk function expression is obtained:

$$F(R_\infty) = \frac{(h\nu - E_b)^\eta}{h\nu} \quad (\text{Eq. 4})$$

$$(F(R_\infty)h\nu)^{1/\eta} = h\nu - E_b \quad (\text{Eq. 5})$$

Where $h\nu$ is the energy of the incident photon and E_b is the optical absorption edge energy, the exponent depends on the type of optical transition caused by photon absorption. By plotting the modified Kubelka-Munk function $(F(R_\infty)h\nu)^{1/\eta}$ as a function of $h\nu$ (Eq. 5) and extrapolating the linear part of the curve in the low-energy region, it is possible to determine the edge energy values which provide information about the oxidation state and environment of the species involved in these optical transitions. For this study, direct transitions were considered, so $\eta = 1/2$.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos Axis Ultra HAS spectrometer with a hemispherical analyzer and Mg K α X-ray radiation source ($h\nu = 1253.6$ eV) operated at 10 mA and 15 kV. The binding energies in the photoelectron spectra were referred to that of C 1s (BE = 285.0 eV).

^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a Bruker 400 MHz spectrometer equipped with a magic angle spin probe at room temperature. The rotor turning speed used was 7 kHz. The calibration for the ^{27}Al core was done with the high-power decoupled (HPDEC) method. The sample used as reference was $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, with a spin rate of 10 kHz, 100 scans at 22.2 °C, and a relaxation time between each pulse of 4 seconds.

3. Results and Discussions

3.1 Textural and Structural

Both the nominal and measured Al contents of the prepared samples, determined by XRF, EDX, and XPS, are presented in Table 1. The raw data from these analyses are presented in Table S2, while the EDX spectra are shown in Fig. S3, both in the supplementary material. The average Si/Al molar ratios of the final products determined by these techniques were quite similar to each other and close to the nominal values stipulated in the initial synthesis gel. These results indicate that the “pH adjusting” preparation method is effective in achieving almost complete incorporation of the aluminum atoms into the mesostructure. It is inferred then that the materials were quite homogeneous, presenting a surface composition similar to that of the bulk sample. This feature is commonly found in Al-SBA-15 samples prepared by the direct synthesis method.

Table 1. Elemental composition of the materials.

Sample	Si/Al molar ratio nominal (gel)	Si/Al molar ratio of final product ^a		
		XRF	EDX ^b	XPS
SBA-15	∞	n.a. ^c	n.a. ^c	n.a. ^c
SBA-15 SiAl 15	15	11.4	15.1	11.5
SBA-15 SiAl 10	10	8.5	10.0	9.4
SBA-15 SiAl 2	2	2.5	2.1	2.1

^a The actual Si/Al molar ratio in the calcined products measured by XRF, EDX, and XPS.

^b SEM-EDX (Supplementary Information).

^c n.a.= not applicable.

The textural characteristics of the SBA-15 materials revealed by N₂ adsorption-desorption are summarized in Table 2. Fig. 1 shows clearly typical type-IVa isotherms according to IUPAC classification [61]. However, both the pronounced capillary condensation step and the formation of different hysteresis loops varied as the Si/Al molar ratio changed. The hysteresis loop for the SBA-15 sample was almost vertical to the axis of relative pressure, presenting a typical H1-type shape, which strongly suggests the existence of large cylindrical pores and that SBA-15 had a highly ordered pore structure [34, 48]. In contrast, at highest levels of Al in SBA-15 result in steeper adsorption/desorption branches and deformation of the hysteresis loop. The adsorption-desorption branches in the Al-SBA-15 samples gradually become almost horizontal in a wide range of P/P_0 , and change to H3 type at higher aluminum loadings, implying that pore shape changes from cylindrical to slit-like channels [62]. Aluminum incorporation changed the pore shape from

cylindrical to slit-like channels, that can be attributed to the assembly of Al species in the mesopores of SBA-15 until pore collapse occurs [63], suggesting a reduction in the textural uniformity of the mesoporous material by the formation of particle aggregates at higher Al loadings [48]. Furthermore, the shape of the hysteresis loop at Si/Al molar ratios lower than 10 suggests the existence of intraparticle pores, i.e., the formation of cavities or voids. The aluminum-containing samples exhibit a similar specific surface area ($370\text{--}380\text{ m}^2\cdot\text{g}^{-1}$), however, these values are lower than that of the pure mesoporous silica SBA-15 ($525\text{ m}^2\cdot\text{g}^{-1}$). This maintenance of the specific surface area around $370\text{ m}^2\cdot\text{g}^{-1}$ could be due to the distortion of the mesoporous channels generated by the deposition of Al species on the inner walls of SBA-15.

The pore size distribution becomes narrower as Al is incorporated into the wall of SBA-15 as indicated by the typical BJH curves of Fig. 2 b) and summarized in Table 2 since SBA-15 has a much wider pore size distribution. Also in Fig. S4 are presented the BJH adsorption and desorption average pore diameter porous size distribution. Likewise, the average pore diameter shows the same trend, decreasing from 8.4 to 5.1 nm for the samples SBA-15 and SBA-15 SiAl 2, respectively. This agrees with the shift of the closure of the hysteresis loop towards lower relative pressures observed in the adsorption isotherms as well as with the decrease in the total pore volume from 1.1 to $0.5\text{ cm}^3\cdot\text{g}^{-1}$. Koekkoek et al. [64] employed different synthesis approaches for a SBA-15 series of aluminosilicates with Si/Al ratio between ∞ and 14 and they observed an increase in the average mesopore diameter from 5.4 to 6.7 nm, respectively. In some cases [23, 25, 65], as in the work by Koekkoek et al., it is observed that the pore size of SBA-15 is increased after metal-incorporation. However, since SBA-15 has an amorphous structure, both the angle and the length of the new M-O bonds could be random and no regular behavior in the modification of the structure and pore diameter can be observed [26, 63]. There are two possible ways of Al incorporation into the SBA-15 structure: 1. Isomorphic substitution of Si^{4+} ions by Al^{3+} ions in the walls of the SBA-15 channels and, 2. Reaction of Al-containing species with silanol groups of the SBA-15 channels. The latter process leads to the narrowing of the pores during the calcination stage of the precursor material [26, 66]. Thus, the observed narrowing of the pore size in our case may be an indication that the incorporation of the aluminum species mostly takes place via interaction of surface groups inside the mesoporous channels during the alumination process. This can be proceeded by a condensation reaction between Al-OH and Si-OH groups on the silica walls which causes the narrowing of the pores [12, 26], or by partial substitution of Si atoms at low Al loadings. At high Al loadings, the formation of aluminum oxide species (Al_xO_y) in the mesopores can also occur [64, 67]. In addition, dS/V ratios were calculated to study the deviation of our materials from the typical behavior exhibited by porous materials with a simple circular or hexagonal geometry. As has been reported in the literature [63, 68], using the structural data of the materials and correlating them by the dS/V ratio, where d , S and V correspond to pore size, specific surface area and pore volume, respectively, it is

possible to elucidate the presence of microporosity in the structure. Normally, when the pore structure presents this type of regular circular or hexagonal geometry, dS/V exhibits values between 4 and 4.2. This is the case of these samples, as shown in Table 2, which indicates that all the materials prepared present an absence of microporosity or its contribution to the texture of the materials is negligible. Despite this, it is recognized that SBA-15 inherently has microporous interconnections between mesopores, which has been proven in the literature, including works reported by Jaroniec et al. [69]. In addition Fajula et al., [70] also reported that SBA-15 without micropores could be synthesized for temperatures as high as 130 °C.

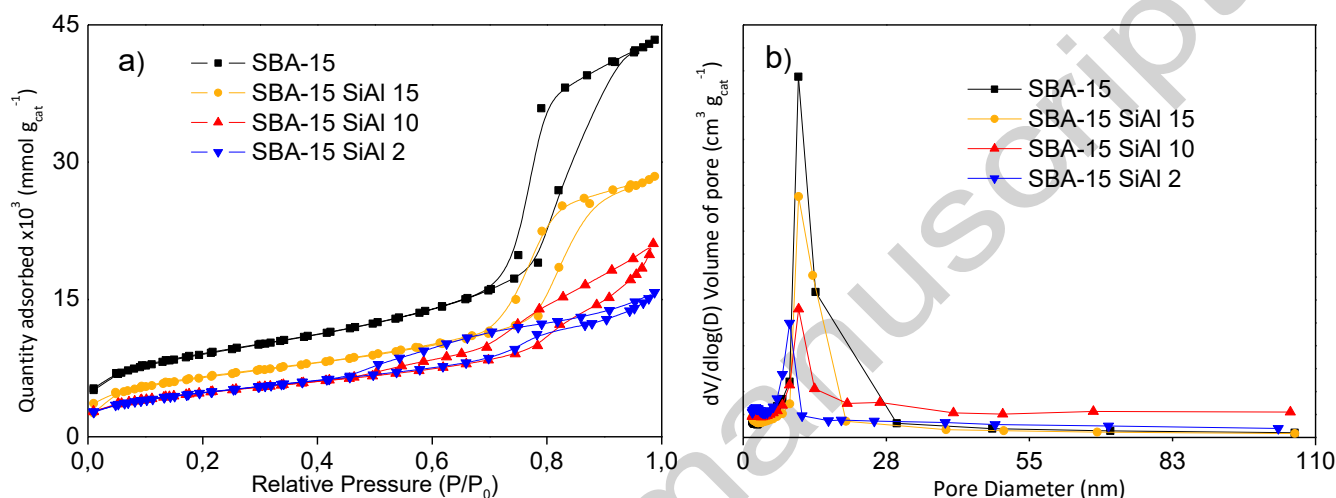


Fig. 1. a) N_2 adsorption-desorption isotherms and b) pore size distribution curves of the materials.

Table 2. Physicochemical properties of the synthetic materials determined by nitrogen adsorption-desorption and XRD measurements.

Sample	BET ($m^2 \cdot g^{-1}$)	V_p^a ($cm^3 \cdot g^{-1}$)	d_p^b (nm)	d_p^c (nm)	d_p^d (nm)	d_{100}^e (nm)	a_0^f (nm)	w^g (nm)	dS/V
SBA-15	525	1.1	8.4	8.4	9.8	9.4	12.3	3.9	4.0
SBA-15 SiAl 15	382	0.7	7.5	7.5	8.7	8.4	13.2	5.7	4.1
SBA-15 SiAl 10	374	0.6	6.6	6.6	8.9	8.0	13.0	6.4	4.1
SBA-15 SiAl 2	381	0.5	5.1	5.1	6.3	5.5	12.2	7.1	3.8

^a Pore volume calculated at $P/P_0 = 0.95$.

^b Adsorption average pore width (4V/A by BET).

^c BJH adsorption average pore diameter.

^d BJH desorption average pore diameter.

^e Interplanar distance of (100) reflection.

^f Unit cell length ($a_0 = 2 \times \frac{d_{100}}{\sqrt{3}}$).

^g Pore wall thickness: $w = a_0 - d_p$.

The structural features of the mesoporous materials were studied through low-angle XRD (Fig. 2 a). The SBA-15 sample exhibits three well-resolved diffraction peaks assigned to (100), (110), and (200) reflections associated with the 2D-hexagonal symmetry ($P6m$) of the SBA-15, revealing the high degree of structural organization of this material [34]. However, in the aluminum-containing samples, the intensities of the

diffraction peaks gradually decrease with increasing Al content. Even the (110) and (200) reflections in the XRD pattern of SBA-15 Si/Al 2 were greatly reduced, indicating a loss of the long-range ordering of the mesoporous structure [48]. This is because the Al species added to the gel mixture could affect the interaction between surfactants and silicates, resulting in the formation of a relatively disordered surfactant-silicate mesostructure [71]. From this finding, it is inferred that Al species are being incorporated in the matrix of SBA-15. In addition, a slight shift of the basal diffraction peak to lower 2θ angles is identified for the sample with a Si/Al = 15 molar ratio and subsequently occurs a slight displacement at wide-angle with higher Al contents, suggesting an initial expansion followed by a contraction of the framework. The initial shifting of the Bragg angle to a slightly lower value indicates that some Al^{+3} species enter into the lattice of SBA-15, leading to the formation of Al-O-Si entities and an increase in the lattice parameters (the larger ionic radius of Al^{+3} (0.054 nm) than Si^{+4} (0.040 nm) leads to longer Al-O than Si-O bond length) [72]. In contrast, the diffraction peak shifts to a higher 2θ angle when the molar ratio is lower than 15, suggesting the contraction of the silica framework [13]. In fact, the calculations of the unit cell parameter a_0 (Table 2) indicate that the values do not follow a linear trend as a function of Al content, it increases at the initial Al incorporation, reaching a maximum value of 13.2 nm at Si/Al = 15 molar ratio, indicating an expansion of mesopores, followed by a decay to 12.2 nm as the Si/Al molar ratio reaches a value of 2. This behavior suggests an initial substitution of Al atoms in the framework of mesoporous silica and subsequently Al_xO_y cluster forms on the surface of the mesopores at low Si/Al molar ratios (high Al content).

Changes in the lattice parameter of SBA-15 as a consequence of Al incorporation have been reported in the literature. In most studies, it was shown to increase due to the difference between the Al-O and Si-O bond distances (as discussed above) [23, 48, 64, 67, 73, 74]. In other reports, however, the opposite trend was observed; with the increasing amount of aluminum incorporation into the SBA-15 structure, the lattice spacing gradually decreased [11, 75]. Kumaran et al. [23] for example, reported that the a_0 increased from 11.9 to 12.6 nm when the Si/Al ratio varied from ∞ to 11.4. In contrast, Wu et al. [30] reported a decrease in the d_{100} spacing from 10.6 to 9.9 nm as the Si/Al ratio was decreased from 80 to 10; however, the lattice spacing rises when the Al content is further increased (from 10 to 2). Thus, previous works report different findings on the variation of the a_0 with increasing Al content. Here, we find that the lattice parameter of our SBA-15 materials showed a strong dependence on the Al content: in samples with Si/Al ratios of 15 and 10 it increased, while for the sample with a Si/Al ratio of 2, it decreased to the value of Al-free SBA-15. Since the synthesis procedure adopted in our work is closer to that reported by Wu et al. ("pH adjusting" method), the reason why the opposite behavior was observed here is not clear and will require further investigation [66].

Wide-angle XRD patterns of the samples are presented in Fig. 2 b). A broad peak at 2θ around 23.5° was observed for all samples, and it is characteristic of amorphous silica. No diffraction peaks ascribed to crystalline reflections of Al_2O_3 or $\text{Al}(\text{OH})_3$ phases were observed in any samples, even for the higher Al loading one, suggesting a highly dispersed or amorphous state for the aluminic species [26, 52, 76].

The diffraction results indicate that the structure of SBA-15 is influenced by the Si/Al ratio implying that the interaction between aluminum and silicon compromises the hexagonal symmetry of SBA-15 and, consequently, reduces the structural ordering in small domains [48, 64]. The SBA-15 sample with Si/Al = 2 likely consists of SBA-15-type particles with only a few repeating units perpendicular to the pore axis and the long-range order is weak [64]. At high Al loadings, part of the Al_xO_y particles formed may produce a narrowing of the mesoporous channels, thus compromising the long-range ordering of the SBA-15 structure.

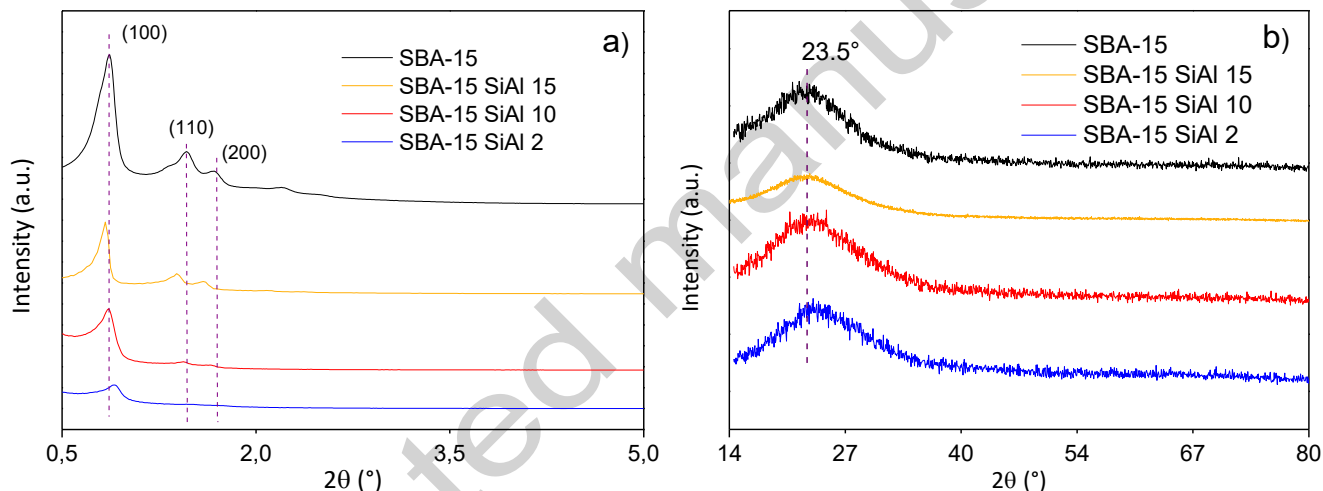


Fig. 2. XRD patterns of SBA-15 samples: a) small-angle and b) wide-angle.

To gain additional information on the structural arrangement and pore architecture of these materials, high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected. A representative image of the SBA-15 sample recorded at low magnification is shown in Fig. S5(A). It shows that the material is very homogeneous and consists of tubular structures up to $2\ \mu\text{m}$ in length and around 100-200 nm in diameter. Fig. 3 (a) exhibits an image of the same sample at higher magnification and reveals that the tubes are curved, and the mesoporous channels run parallel to the surface. The channels are open at both ends as shown in Fig. S5(A). A cross-sectional view of one of the tubes is presented in Fig. 3 (b), which demonstrates an excellent hexagonal arrangement of the cylindrical channels with long-range ordering in SBA-15. The results are in accord with the small-angle XRD patterns and nitrogen sorption isotherms, confirming the

two-dimensional hexagonal structure of this material. The sample with a Si/Al = 10 (Fig. 3 c-d) still shows the channeled structure of SBA-15 with an ordered arrangement of individual channels whose d_{100} -spacing is about 6.5 and 11.5 Å as shown in the Fourier Transform (FT) image inset in the micrograph (Fig. 3 (c)). It is noteworthy that the incorporation of aluminum caused the structural order to decrease, with fragmented particles in several domains. The domains appear randomly oriented and are causing the slight broadening of the low-angle XRD reflections [64]. In addition, an *in-situ* EDX spectrum is presented which reveals the presence of Si, Al, O, and K in the sample and the Si/Al ratio determined was 9.9, quite consistent with the nominal value. The same ratio was obtained on different particles, which supports the idea that Al is incorporated into the structure of SBA-15 in an appropriate manner. It must be noticed that no large aggregates or phases (such as Al₂O₃) blocking the pores were observed, confirming that extra-framework aluminum phases are well dispersed in the mesopores in the aluminum-containing samples [25]. These results underline that the “pH-adjusting” method is highly effective in maintaining the hexagonal arrangement of the cylindrical channels, although the long-range order of this sample is weaker than that of the pure SBA-15. We believe that due to the level of target Al in the initial solution, the insertion of high Al content could induce some loss in the ordered mesoporosity of the SBA-15.

A representative HAADF-STEM image of a low magnification (Fig. S5(C)) of the SBA-15 SiAl 2 sample contains curved particles showing mesostructured channels. From Fig. 3 (e) and (f) the mesoporous nature of the sample is evident. Nonetheless, the existence of multiple randomly oriented domains reveals that the mesostructure presents a short-range order. A large fraction of the tubular pore walls appears damaged and resulting in disordered arrays consisting of small fragments of SBA-15. A decrease in the size of these domains has been known to cause a broadening of the low-angle XRD reflections and points out that this sample has a much more complex structure, which in turn is consistent with the change in the morphology of the material according to the physisorption results. Nevertheless, well-ordered sets of parallel mesopores can still be distinguished locally in the images. On the other hand, it must be noticed that no bulky aggregates or phases associated to Al₂O₃ blocking the pores were observed [25].

The results of XRD at small-angle, N₂ physisorption, and HRTEM clearly substantiate that the incorporation of Al into the SBA-15 structure leads to modification of the morphology and in the ordering degree of the hexagonal structure of the SBA-15 due to the introduction of Al species. The structure order of the parent (Al-free) SBA-15 is compromised in the presence of a low Si/Al molar ratio (i.e., at high Al content the long-range order is weak). The partial loss in the structural regularity of the characteristic structural arrangement of SBA-15 upon the incorporation of high Al loadings can be explained by considering the alumination synthesis process of these materials. The Al species that are present in the form of

tetrahydroaluminate ions after adjusting the pH to 7.5 undergo condensation with the surface silanol groups of SBA-15. Consequently, a large amount of reactive aluminum species in the reaction mixture may hinder this interaction between the template and the Si precursor, thus leading to the formation of SBA-15 silica with lower structural regularity.

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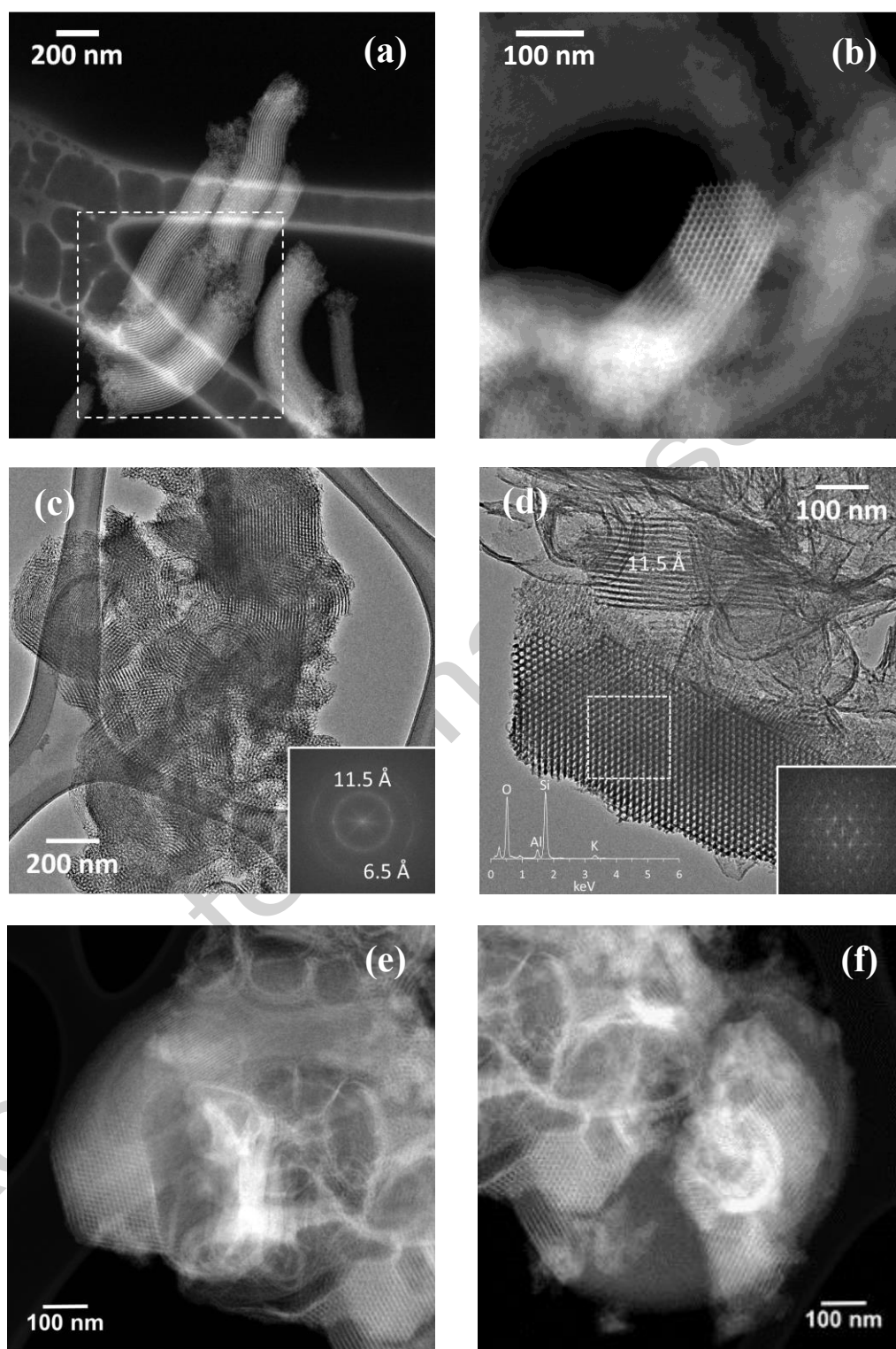


Fig. 3. HRTEM and HAADF-STEM images for the materials: (a)-(b) HAADF-STEM images of the SBA-15; (c)-(d) HRTEM images of the SBA-15 SiAl 10 and (e)-(f) HAADF-STEM images of the SBA-15 SiAl 2.

3.2 Acidity

The acidity of the SBA-15 and aluminum-containing materials was studied by different techniques. Temperature-programmed desorption of ammonia (NH₃-TPD) provides information on the total acidity of the solids. Ammonia is a suitable probe molecule due to its small size and high basicity, which allows it to interact with most acid sites. The NH₃-TPD profiles of the aluminum-containing samples (Fig. S6) are similar, with a desorption peak in the range of 80 to 350 °C, corresponding to acidic sites with weak and medium strength, which increase slightly with decreasing Si/Al molar ratio. In contrast, the profile of SBA-15 does not show a distinctive desorption profile in this range, indicating low acidity due to the presence of only silanol groups. The determination of the total amount of desorbed NH₃ per gram of material (Table 3 and Fig. S6) indeed suggests that the acidity of the samples could be associated with Al species, since pristine SBA-15 does not have considerable acidity [76] and because the concentration of weak acid sites increases with aluminum loading, except for sample SBA-15 SiAl 10 which shows a drop in the amount of NH₃ desorbed.

Table 3. Acidity measurements by NH₃-TPD and Py-FTIR.

Sample	Total acidity by NH ₃ -TPD (μmol·g ⁻¹)	Measurement by Py-FTIR		
		C _{Brønsted} ^a (μmol·g ⁻¹)	C _{Lewis} ^b (μmol·g ⁻¹)	C _{Brønsted/Lewis} ^c
SBA-15	253	0	0	u.d. ^d
SBA-15 SiAl 15	351	21	7	3.0
SBA-15 SiAl 10	202	1	3	0.3
SBA-15 SiAl 2	844	67	43	1.6

^a Concentration of Brønsted acid sites.

^b Concentration of Lewis acid sites.

^c Brønsted/Lewis acid sites concentration ratio.

^d u.d: undefined.

To evaluate the strength and types of acid sites of the SBA-15 samples, pyridine adsorption measurement coupled with FTIR spectroscopy (Py-FTIR) was performed. The Py-FTIR spectra of the samples are shown in Fig. 4 and the distribution of acidic sites calculated quantitatively by intensity measurement is listed in Table 3. The surface acidity of the materials studied is associated with the presence of both Lewis and Brønsted acid sites due to the combination of pyridine ions with the surface acid hydroxyls and the hydrogen-bonding hydroxyls, respectively. The spectrum of pristine SBA-15 only shows two peaks of low intensity at 1440 and 1590 cm⁻¹ which are attributed to pyridine hydrogen bonded to Si-OH groups (Py-HO-Si) [48, 76].

In contrast, on the Al-SBA-15 samples pyridine adsorbed on both Lewis acids sites (1453 and 1619 cm^{-1}), and Brönsted acids sites (1545 and 1637 cm^{-1}) (the IR band at 1491 cm^{-1} belongs to pyridine adsorbed on both Lewis and Brönsted acidic sites) [34, 77]. In addition, the amount of hydrogen-bonded pyridine (Py-phy) decreases and ultimately disappears, indicating that the introduction of higher Al load results in fewer free silanol groups. The aluminum species are incorporated into the SBA-15 matrix by isomorphic substitution in tetrahedral (AlO_4) domains along with the generation of Al in an octahedral environment (non-framework AlO_6) [34]. The isomorphic substitution was achieved in the SBA-15 SiAl 15 sample resulting in fewer free silanol groups due to the almost complete absence of hydrogen-bonded pyridine (Py-phy). In this respect, SBA-15 SiAl 15 sample presents 21 and $7\text{ }\mu\text{mol}\cdot\text{g}^{-1}$ of $C_{\text{Brönsted}}$ and C_{Lewis} , respectively (Table 3). With further increase in the Al loading (i.e., SBA15 SiAl 10 sample), free silanol groups are again visualized due to the presence of the hydrogen-bonded pyridine species. It can be suggested that for this sample the aluminum species were incorporated isomorphically accompanied by a growth of a small number of extra-framework Al species. At this level, it may be produced small aggregates of Al_xO_y species, as suggested by the CO adsorption FTIR spectroscopy results discussed later (Fig. 5). Indeed, this result is also in line with the NH_3 -TPD experiment. This feature can be associated with changes in the regularity of the pore structure promoted by the presence of a higher Al load. In this regard, a fraction of a short-range order contribution starts to appear more markedly in the sample SBA-15 SiAl 10 as evidenced by XRD and HRTEM analysis. The appearance of the short-range order domains may produce breakage of the channels generating new porosity and pore walls, leading to the formation of hydroxyl groups that, in turn, can physically adsorb H-bonded pyridine [48]. The acidity observed for the SBA-15 SiAl 10 can be ascribed to the decreases in the number of isolated Al species and, consequently, in the concentration of acid sites and acidity of the material compared to the SBA-15 SiAl 15.

In the case of the SBA-15 Si/Al = 2 sample, the absorption bands (1491 , 1545 , 1637 cm^{-1}) appear slightly shifted towards higher wavenumber values compared to the other samples, indicating higher quantities and strength of the acid sites. The intensities of the absorption band increase considerably in SBA-15 SiAl 2. The IR absorption bands at 1453 cm^{-1} can be interpreted in terms of the overlapping of two bands attributed to hydrogen-bonded pyridine and Lewis-type adduct [78]. According to Chanquía et al. [78], the band at 1590 cm^{-1} observed for low Si/Al molar ratios shift towards 1619 cm^{-1} for high Si/Al molar ratios and can be assigned to pyridine coordinated to weak Lewis acids sites. On the other hand, Py-FTIR measurements also revealed a change in surface acidity with increasing Al amount. The highest load of Al introduces both Lewis and Brönsted acidity into the SBA-15 structure. In addition, for this sample, a strong loss in the long-range order and the appearance of short-range order in the structure were observed. This may also generate domains with different acidities. At the highest aluminum content, the growth of larger Al_xO_y aggregates is

possible. The ratio between the concentration of Brönsted and Lewis acid sites depends on the Al content (Table 3). The Brönsted/Lewis ratio ($C_{B/L}$) of the SBA-15 SiAl 2 was the highest among the Al-containing SBA-15 samples. However, all samples yet show a higher concentration of Brönsted than Lewis acid sites. The mesoporous aluminosilicates with Si/Al ratios less than 10 result in materials with a higher amount of Brönsted acidic sites.

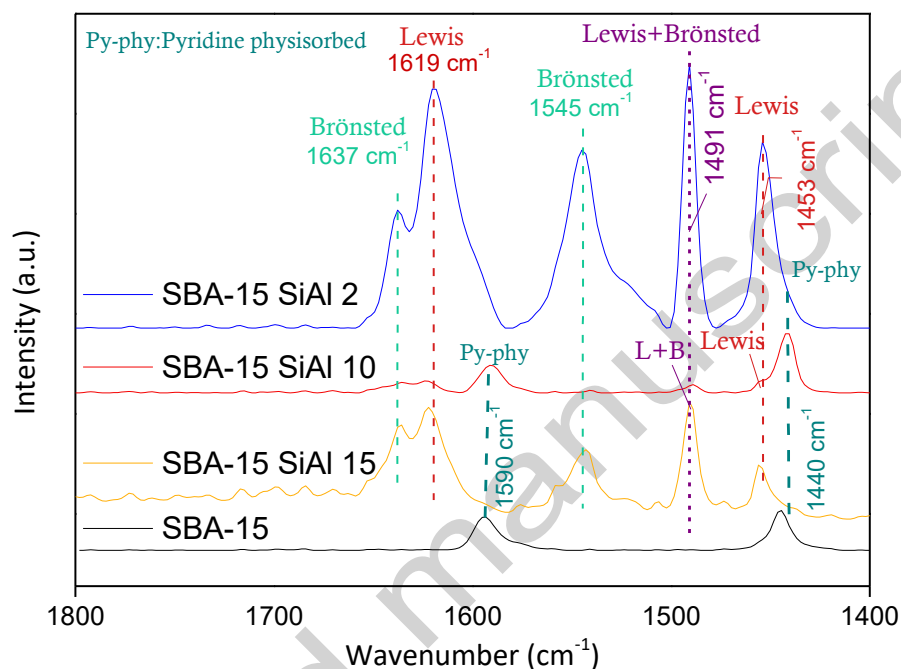


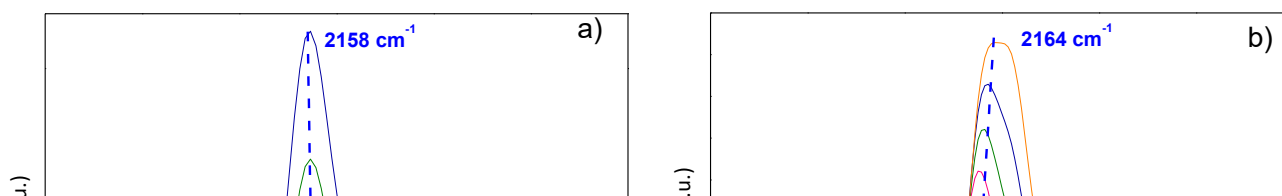
Fig. 4. FTIR spectra of pyridine adsorbed on Al-containing mesoporous SBA-15 silicas materials. (The legend Py-phy present in Fig. is pyridine physisorbed).

CO adsorption FTIR spectroscopy was also used to study the strength and nature of the acid sites of these materials. At low temperatures (-196°C), CO molecules can form hydrogen bonds with Brönsted acid sites causing perturbation in O-H vibrations and also coordination bonds with Lewis acid sites. Fig. 5 displays the series IR spectra of CO collected from a) SBA-15, b) SBA-15 SiAl 10, and c) SBA-15 SiAl 2 in the presence of CO at increasing equilibrium pressures. The spectrum of SBA-15 exhibits two very distinct bands. The band at 2138 cm^{-1} (CO phase condensed in the pores of SBA-15), and at 2158 cm^{-1} (CO adsorbed on the weakly acidic silanol groups) [79, 80]. The low-intensity band at 2110 cm^{-1} represents carbon monoxide coordinated to the silanol group via its oxygen atom. The absence of an IR band at wavenumber $> 2180\text{ cm}^{-1}$ indicated that no Lewis acid sites are present in the Al-free SBA-15 material [79].

In contrast, in the spectra of the Al-containing samples, the IR band representing H-bonded CO molecules shifts from 2158 cm^{-1} to 2164 cm^{-1} at Si/Al = 10 and to 2170 cm^{-1} at the Si/Al = 2. The shift of this band towards higher wavenumbers suggests that the incorporation of aluminum into the SBA-15 matrix generates

new types of acid sites. In the IR spectra of the Al-free SBA-15 (panel a) the position of the band of hydrogen-bonded CO is invariant of CO pressure, underlining the uniform, albeit weak, acidities of the silanol groups. In the spectral series of SBA-15 SiAl 10, the H-bonded CO feature appears at around 2170 cm^{-1} at low P_{CO} partial pressures, and then, as the P_{CO} increases, it shifts toward lower wavenumbers. In addition, this feature also becomes much broader at higher P_{CO} as silanol groups also interact with CO. At the highest P_{CO} studied, the maximum of this peak is located at 2164 cm^{-1} , close to the 2158 cm^{-1} values we have measured for the Al-free SBA-15 samples (panel a). At Si/Al = 2 this peak shifts to an even higher wavenumber at low P_{CO} ($\sim 2176 \text{ cm}^{-1}$) and the feature stays narrow. At the highest P_{CO} , the peak is centered at 2170 cm^{-1} , much lower than the band at 2158 cm^{-1} seen for the Al-free SBA-15. A shoulder with a very intensity can also be seen at high P_{CO} , indicating the presence of a very small amount of Si-OH groups in this sample. The appearance of two additional bands, centered at 2190 and 2230 cm^{-1} is attributed to the coordination of CO to Al^{3+} Lewis acid sites on the surface of the SBA-15 SiAl 2. The appearance of these two extra features indicates that at these high Al contents, not all Al^{3+} ions got incorporated into the SBA-15 structure but formed Al_xO_y clusters in the mesopores.

In the case of the Si/Al = 10 sample, there is only one at 2230 cm^{-1} , a low-intensity feature that can be assigned to Lewis acidic Al^{3+} bond CO molecules. However, at Si/Al = 2 (high Al content) a large amount of extra-framework Al^{3+} ions are present exhibiting different coordinations that are manifested by the two distinct CO vibrational frequencies at 2190 and 2230 cm^{-1} [33]. Therefore, the decrease in both the concentration of acid sites and total acidity that was evidenced by the Py-FTIR and NH_3 -TPD results for the Si/Al = 10 sample ratio can be explained by the formation of small Al_xO_y aggregates produced by the appearance of short-range order domains that may generate different acidities as suggested by the weak band at 2230 cm^{-1} obtained in the CO-FTIR spectrum.



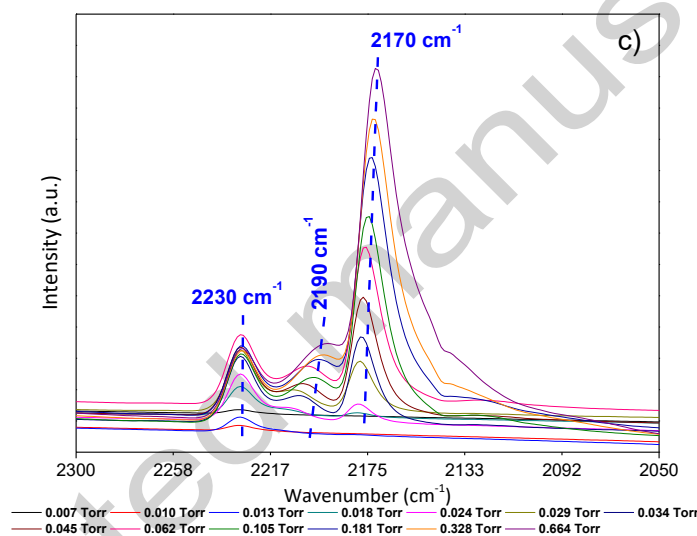


Fig. 5. FTIR of CO adsorbed at -196 °C on Al-containing mesoporous SBA-15 silicas materials: a) SBA-15, b) SBA-15 SiAl 10, and c) SBA-15 SiAl 2.

The nature and distribution of hydroxyl species in Al-SBA-15 materials were studied by FTIR spectroscopy and compared with pure silica SBA-15 (Fig. 6). The FTIR spectra of all samples are almost the same with slight variations. The bands at 3461 and 1632 cm^{-1} are assigned to -OH stretching (ν) vibrations of silanol groups and -OH bending (δ) modes of adsorbed H_2O , respectively. All samples display four absorption bands at 1073 with a shoulder at 1227 cm^{-1} , 953, 795, and 460 cm^{-1} which are attributed to Si-O-Si stretching (ν), Si-OH stretching (ν), T-O stretching (ν) (T = Si or Al) and Si-O-T bending (δ) modes vibration, respectively [76, 81]. The band at 953 cm^{-1} exhibited by the pristine SBA-15 disappears once aluminum is added. This means that the introduction of Al results in the reduction of the number of silanol groups present in SBA-15 due to the condensation of the Al species with the silanol groups [76]. In addition, the presence

of the band at 795 cm^{-1} which is assigned to the vibration of $[\text{SiO}_4]$ units bonded to heteroatoms may be an evidence of the existence of metal ions incorporated in the structure.

On the other side, in qualitative terms the intensity of the band at 1073 cm^{-1} in the SBA-15 SiAl 10 sample is much higher than in the other samples, suggesting a higher population of Si-O-Si. It is also possible to note a variation in the intensity of the absorption bands at 3461 cm^{-1} and 1632 cm^{-1} upon the incorporation of Al into the material. This can be interpreted as a higher capacity of absorption of the humidity of the environment due to the higher population of acid sites generated by the introduction of Al. A shift of these absorption bands towards a lower wavenumber was also noticed with the incorporation of Al species, indicating that strong interactions between silicon and Al atoms were formed, such as the formation of Si-O-Al bonds. This is indeed explained by the fact that the length of the Al-O bond is longer than the Si-O bond which leads to a decrease in the force constant and hence a decrease in the vibrational frequency, calculated from the formula $\nu = (\frac{1}{2}\pi c)\sqrt{k/u}$ [63].

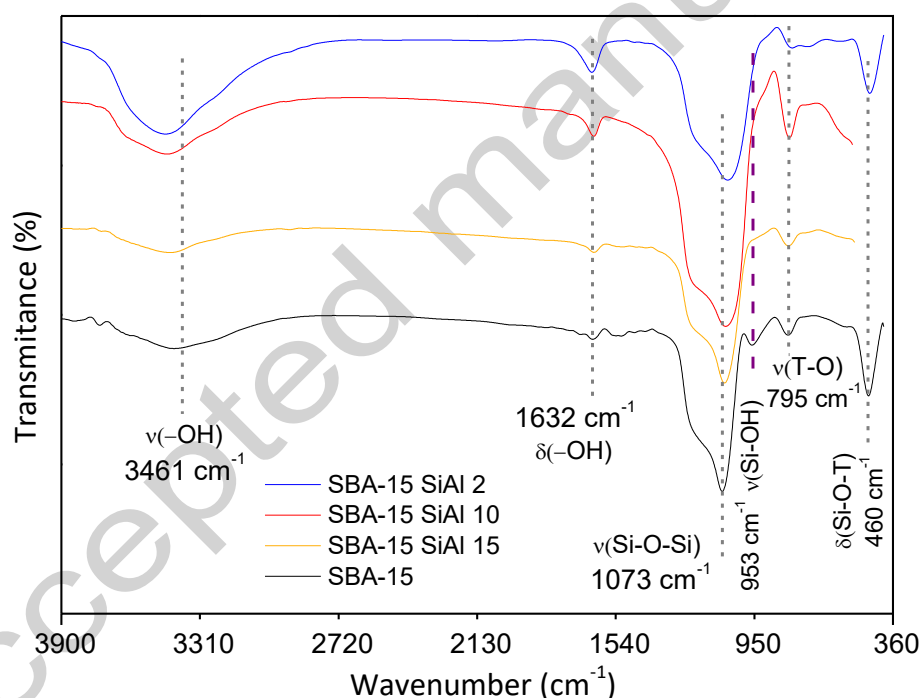


Fig. 6. FTIR spectra of SBA-15 samples containing aluminum.

Fig. 7 shows the IR spectra in the hydroxyl range of the samples after calcination at $150\text{ }^{\circ}\text{C}$ under argon flow. The IR spectrum of pure silica SBA-15 presents one asymmetric and intense band at around 3739 cm^{-1} . The spectra collected from the Al-containing samples are also dominated by this absorption band but its intensity decreases as the Si/Al molar ratio decreases. The peak position of the shoulder band centered at around 3679 cm^{-1} in the spectrum of the SBA-15 sample gradually red shifts with increasing Al incorporation, and it is recorded at 3573 cm^{-1} in the SBA-15 SiAl 2 sample. According to prior reports, the

band at 3739 cm^{-1} is attributed to the $\nu(\text{O-H})$ stretching vibration of isolated silanol groups, as it is typically observed for silica and aluminosilicates [64, 82]. The decrease in the intensity of this band indicates that the incorporation of larger amounts of Al by the “pH-adjusting” method results in the reduction in the number of Si-OH groups, a direct consequence of their progressive consumption in the condensation reactions with hydrolyzed Al atoms [25]. The broad absorption feature in the $3680\text{--}3400\text{ cm}^{-1}$ spectral range is correlated with overlapped bands typical of weakly acidic H-bonded OH groups. The interaction between vicinal OH groups (i.e., Si-OH, H-OH, and Al-OH groups) is responsible for this broad band representing perturbed Si-OH sites [25, 83]. Therefore, the behavior observed for the aluminum-containing samples indicates the alteration in the distribution of the OH groups after the incorporation of Al in SBA-15, in agreement with the formation of new interactions suggested by the previous IR spectra (i.e., Fig. 6). Hence, the broadening of the band contribution between $3680\text{--}3400\text{ cm}^{-1}$ is then attributed to the formation of neighboring silanol nests because of the perturbation generated by the Al species introduced into the material, which are involved in the condensation processes between silanol and aluminol groups.

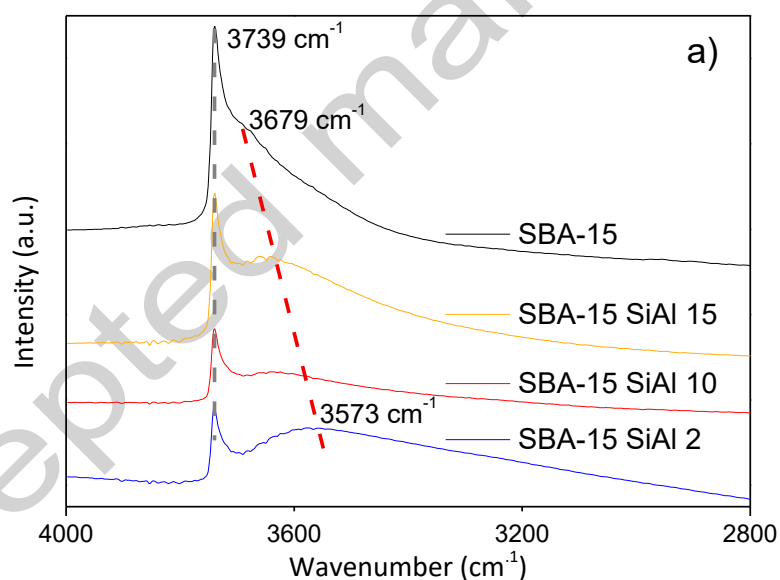


Fig. 7. OH region of FTIR spectra on Al-containing mesoporous SBA-15 silica materials after thermal treatment at $150\text{ }^{\circ}\text{C}$ in Ar flow.

Along these lines, we argue that the main mechanism of aluminum incorporation was the isomorphic substitution of Si^{4+} ions by Al^{3+} ions. Aluminum ions are preferentially introduced into the silica framework and dispersed along the mesopores to form tetra-coordinated centers [26, 63]. From the decrease in pore diameter that was observed by N_2 -physisorption, it is possible to postulate that the surface silanol groups of

the preformed structure can react with some Al species into the solution during the synthesis process and thus part of the Al species condenses with the silanol groups to form four-coordinated aluminum on the surface, reducing the pore size. Simultaneously part of the Al ions builds into mesoporous walls, settling to the interior of the silica framework also in a tetrahedral environment to form Si-O-Al linkages, producing the unit cell parameter variation as seen by XRD [13, 26]. Subsequently, when an additional amount of aluminum is loaded, during the alumination process the metal ions could not be substituted into the silica framework and are deposited on the external surface of the pore in the so-called corona region [26]. This leads to partial co-condensation between the aluminum species already present on the surface with tetrahedral coordination (AlO_4) and with the residual silanol groups to form non-framework Al_xO_y that consequently, leads to the pore narrowing. Effectively, the decrease of the intensity of the band associated with isolated silanols and the gradual change in the distribution of OH groups that were observed by FTIR spectroscopy (region of OH stretching vibrations) with decreasing Si/Al ratios confirm the deposition of the metal ions. The reduction of the Si-OH groups is related to their progressive consumption in the condensation reactions with the hydrolyzed $\text{Al}(\text{OH})_x$ species.

3.3 Spectroscopic analysis

Insights about the coordination environment of ionic species in the samples were obtained by UV-Vis Diffuse Reflection spectra (UV-Vis DRS) as shown in Fig. 8. The UV-Vis DRS spectroscopic technique is widely used to distinguish the framework and extra-framework aluminum species [84]. The absorption band at approximately 240 nm is typically attributed to the silica structure of SBA-15 synthesized under low pH values [66, 85, 86]. The Al-SBA-15 materials showed an absorption band centered at ca. 241 nm related to the Al-O bond, which is due to the oxygen-to-metal charge-transfer transitions of four-coordinated framework aluminum characteristic of the alumina-silica structure of Al-SBA-15 [66]. It must be added that SBA-15 SiAl 10 and SBA-15 SiAl 2 materials present a shoulder at ca. 270 nm together with the main band at 242 nm. The 270 nm band is attributed to the formation of extra-framework aluminum [87].

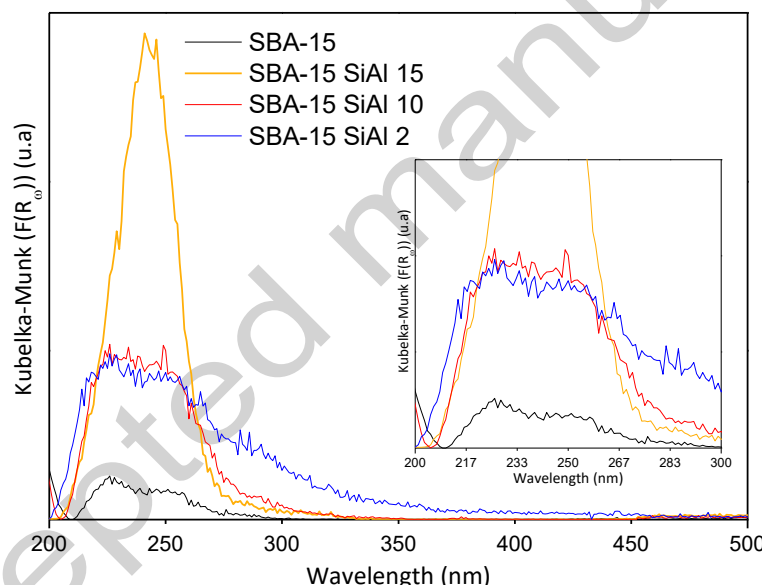


Fig. 8. UV-Vis diffuse-reflection spectra of SBA-15 and Al-SBA-15 materials.

Furthermore, in Fig. 9 the plots of the Kubelka-Munk function as a function of the incident photon energy for the SBA-15 and Al-SBA-15 series of materials are presented. These plots were used to determine the variation of the edge energy with the Si/Al molar ratio. The edge energies, determined from these plots, decrease as the Si/Al molar ratio in the materials decreases, which explains the slight shift towards the longer wavelength of the bands observed in the UV-Vis DRS spectra in Fig. 8. This allows us to propose that Al species induce an enhancement in the electronic mobility of SBA-15, decreasing the band-gap of the material. This means that it improves the electrical properties and the semiconducting character of the system suggesting some interaction between Al and Si species [88].

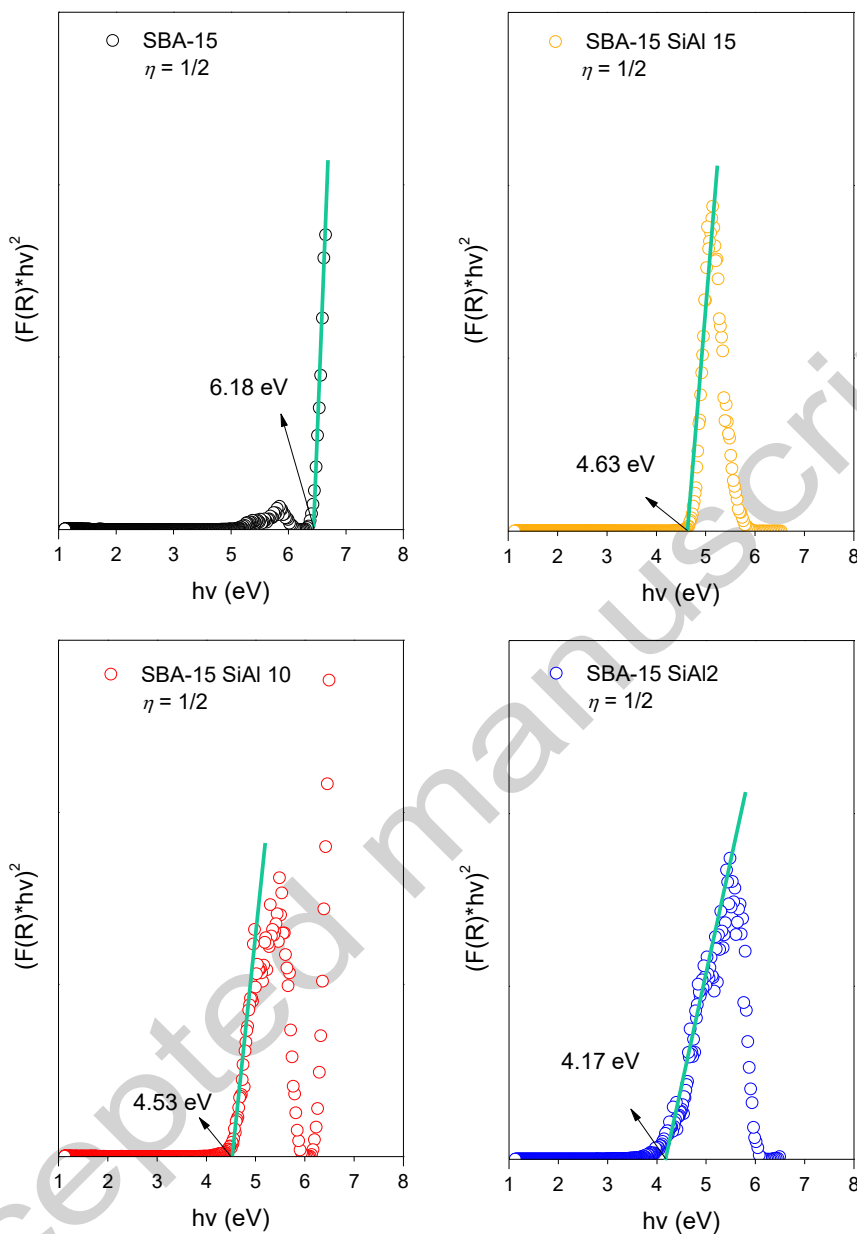


Fig. 9. Kubelka-Munk plot for SBA-15 and Al-SBA-15 materials.

To obtain more information on the surface composition of the mesoporous materials XPS was used (Fig. 10). Fig. S7 shows the survey scan of SBA-15 and aluminum-containing materials. Peaks at 100.7 and 151.8 eV were assigned to the characteristics Si $2p_{3/2}$ and Si 2s orbitals in silica materials. The presence of the strong O 1s spectral line at around 530 eV and a weak spectral line at 22 eV represents oxide ions in metal oxide (i.e., SiO_2 , Al_xO_y) [66]. The peak observed at 117.1 eV in SBA-15 SiAl 2 sample corresponds to the binding energy of the 2s orbital of aluminum (Fig. 10d), assigned to Al^{3+} ions in octahedral sites.

The narrow scan XPS spectra with the binding energies of O 1s, Si $2p_{3/2}$, and Al 2p are presented in Fig. 10. Table 4 shows the binding energy (BE) values obtained for Al 2p, Si 2p, and O 1s and the Si/Al atomic

ratios determined by XPS. From the surface Si/Al molar ratios determined by XPS, it can be inferred that the materials are quite homogeneous, presenting a surface composition similar to the bulk phase. The Si 2p and O 1s signals are symmetrical and centered at ca. 103.5 and 532.6 eV which agrees with the corresponding signals of these elements in these types of compounds [67].

The O 1s spectra of the SBA-15 sample had a binding energy of 532.9 eV, which approaches the binding energy value of 533.0 ± 0.2 eV reported for pure SiO₂ [89]. With the introduction of aluminum species, the development of a feature at about 531.2 eV was observed. The intensity of this component progressively grows with the introduction of aluminum species from 7.6% for the SBA-15 SiAl 15 to 29.6% for the SBA-15 SiAl 2 sample (Table 5). This may suggest some interaction between oxygen species with Al.

With respect to the Si 2p binding energies, a shift towards lower energies is observed as Al is introduced into the mesoporous silica. This shift can be attributed to the presence of Si-O-Al species in the SBA-15 structure [76]. It must be added that not only the main peak Si 2p shifts to lower binding energy values (Table 4) but the intensity ratio between the deconvoluted peaks (Table 5) changes as well with the increase in the load of aluminum species. Indeed, when the aluminum species were introduced, the binding energy of the Si-O-Si bond was shifted slightly to lower values due to oxygen gaining electrons from Al, causing a change in a core electron of oxygen. These perturbations of the peaks to lower binding energies indicated that the Al species was successfully incorporated into the samples.

The Al 2p peak appears at 74.4 eV for SBA-15 SiAl 15 and 74.3 eV for SBA-15 SiAl 10. Meanwhile, a binding energy of 74.8 eV was observed for SBA-15 SiAl 2 sample. Cazalilla et al. [67] reported three binding energies of Al 2p with values of 73.0, 74.5, and 75.4 eV, which were assigned to pure Al, Al_xO_y, and Al₂O₃, respectively. According to these records, binding energy values on the 74.3-74.8 eV interval can be ascribed to Al_xO_y (x:y = 3:1 or 1:1) species, where Al is less oxidized than the Al₂O₃ phase. It should be noted that in the sample with the lowest Si/Al ratio, its signal slightly shifts to higher energy values. This indicates that at Si/Al > 2 ratios the aluminum species are principally anchored within the porous matrix of SBA-15 by reaction with the silanol groups during synthesis. While at Si/Al = 2 ratio the aluminum is found in high oxygen coordination (Al_xO_y x:y = 3:1) compared to the other samples, possibly formed on the outer surface. Besides, the Si/Al surface atomic ratio for all aluminum-containing materials was close to the nominal load (Table 1). The latter was expected since the “pH adjusting” method implicates the Al resource being added to the reaction mixture, involving co-assembly and direct condensation of the active phase.

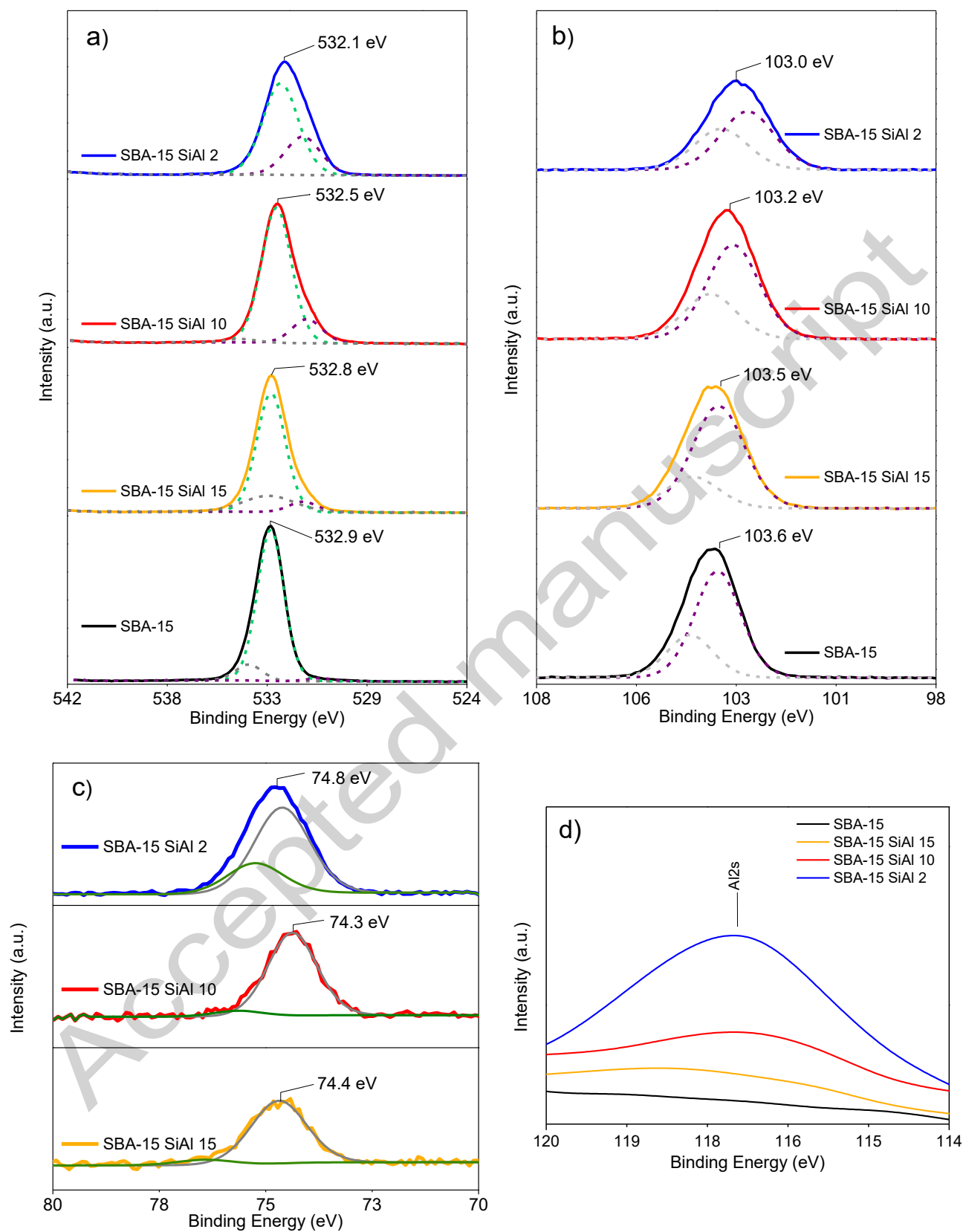


Fig. 10. XPS spectra of a) O 1s; b) Si 2p; c) Al 2p and d) Al 2s for SBA-15 and Al-SBA-15 materials.

Table 4. Binding energies (BE) and surface Si/Al atomic ratio in the SBA-15 materials.

Sample	Binding energy (eV)			Si/Al
	Al 2p	Si 2p	O 1s	
SBA-15	-	103.5	532.8	-
SBA-15 SiAl 15	74.4	103.5	532.8	11.6
SBA-15 SiAl 10	74.3	103.2	532.6	9.5
SBA-15 SiAl 2	74.8	103.0	532.2	2.1

Table 5. XPS spectra deconvoluted peaks.

Sample	Binding energy (eV)		
	O 1s	Si 2p	Al 2p _{3/2}
SBA-15	530.6 (1.8%)	103.5 (71.4%) 104.2 (28.6%)	n.a. ^a
	532.8 (88.9%)		
	533.8 (9.3%)		
SBA-15 SiAl 15	531.2 (7.6%)	103.4 (76.4%)	74.7 (92.0%)
	532.8 (3.7%)	104.1 (23.6%)	76.4 (8.0%)
	532.9 (88.7%)		
SBA-15 SiAl 10	531.2 (14.8%)	103.1 (67.6%) 103.6 (32.4%)	74.4 (93.5%) 75.6 (6.5%)
	532.6 (83.2%)		
	534.19 (2.0%)		
SBA-15 SiAl 2	531.4 (29.6%)	102.8 (58.8%)	74.6 (73.6%)
	532.4 (70.4%)	103.4 (41.2%)	75.2 (26.3%)

^a n.a. = not applicable.

The ²⁷Al MAS NMR spectroscopy was carried out to demonstrate the change of coordination state of Al species in Al-containing mesoporous SBA-15 (Fig. 11). The spectra of the SBA-15 SiAl 15 and SBA-15 SiAl 10 samples display a sharp resonance peak at 53 ppm, which is assigned to 4-coordinated Al species in the SBA-15 framework (AlO₄ structural unit) [77]. There are no signals located in this region of spectra related to other Al species, consequently, this suggests that most Al atoms were incorporated by isomorphic substitution of Si⁴⁺ cations in the SBA-15. Meanwhile, in the spectrum of the SBA-15 SiAl 2 sample, the appearance of a low intensity at 0 ppm is clearly distinguished. This resonance line is associated with octahedral-coordinated Al species (AlO₆ structural unit) in extra-framework positions [25, 34].

Since the diffraction patterns of this sample did not exhibit peaks associated with alumina phases in XRD nor were large Al_2O_3 aggregates evident in the HRTEM images, it is inferred that the extra-framework aluminum species are well dispersed in the mesopores and on the external surface. It should also be noted that no contributions associated with penta-coordinated aluminum species were observed due to the absence of signals at around 30 ppm, so the atoms introduced by the "pH adjusting" method were exclusively localized as tetra-coordinate and hexa-coordinate species.

In summary, these results imply that a large part of the Al species is mainly incorporated and dispersed into the silica structure during this synthesis procedure, even at high loadings of Al, which is consistent with the distribution suggested by XPS and XRD. Based on these observations, it is possible that initially at low levels of Al, they are located in tetrahedral coordination sites within the mesoporous walls of the material, covalently bonded to four Si atoms by oxygen bridges. Then, when the Al concentration in the reaction mixture is very high ($\text{Si/Al} < 10$) the Al species preferentially adopt the extra-framework positions depositing on the primary AlO_4 units previously formed, leading to the formation of Al_xO_y . This is in line with the above-described findings from Py-FTIR characterization where an increase in the proportion of Lewis acid sites was observed which is associated with the external and deficiently coordinated Al species. Additionally, the gradual increase in the AlO_4 content detected by ^{27}Al MAS NMR is consistent with the gradual increase in the intensity of the broad band at $3680\text{--}3400\text{ cm}^{-1}$ seen by FTIR (Fig. 7) suggesting that the contribution to this band may come from the Al-OH groups. The combination of these species in different coordination environments could explain the variation of lattice parameters, pore size, and formation of acid sites in the SBA-15 system, which was discussed above.

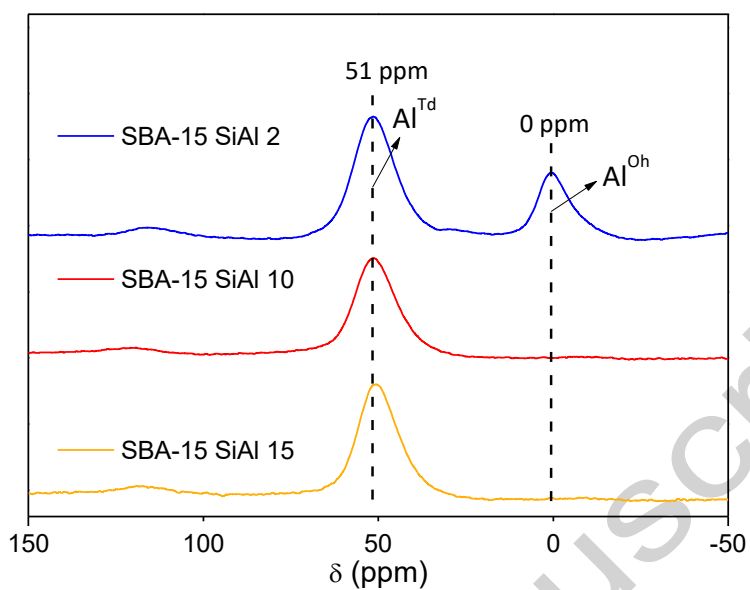


Fig. 11. ^{27}Al MAS NMR spectra of Al-SBA-15 samples with different Si/Al ratios. Td: tetrahedrally coordinated aluminum species. Oh: octahedrally coordinated aluminum species.

4. Conclusions

A series of mesoporous SBA-15 materials with different Si/Al molar ratios (Si/Al = 15, 10, and 2) were prepared by the “pH-adjusting” method. The incorporation of aluminum species affected the textural, structural, and acidity of the materials. On the textural side, the formation of different hysteresis loops was observed as the Si/Al molar ratio changed. Even at high aluminum contents, the materials obtained were mesoporous, confirmed by the presence of the characteristic type IV N₂-physisorption isotherms. The results of X-ray diffraction and high-resolution electron microscopy measurements indicated that above a certain level of aluminum loading the long-range structural organization was compromised, although the mesopore structure was preserved. The variation of the Al content locally preserved the local hexagonal arrangement of the parallel mesochannels of SBA-15. However, an introduction of high Al loading (Si/Al < 10) into the silica materials would result in the loss of the typical long-range ordered mesopores of the SBA-15. The pore size and pore volume decrease with an increase in the Al content, meanwhile the interplanar distance and hexagonal unit cell did not follow a linear tendency with the change of the Al concentration in the samples. This phenomenon has been widely discussed in the literature for materials synthesized by different methods [34, 77], (including “pH adjusting” [25, 73]), as opposite trends that have been observed when the Si/Al molar ratio was further decreased. Differences in the location of sites introduced species are caused by the amorphous character of SBA-15 in which the bond angles and bond lengths vary. Therefore, the incorporation of metal ions does not follow a regular rule and causes variations in the observed textural and structural parameters. Insights about the incorporation of aluminum species were obtained from spectroscopic analyses such as CO adsorption FTIR, UV-vis DRS, and XPS. XPS spectra of Al 2p suggest the Al species are less oxidized than in the Al₂O₃ phase providing some sign of Al incorporation into the SBA-15 framework. The ²⁷Al NMR results revealed that the Al species present in the initial gel were incorporated into the final material and a substantial portion of them are part of the mesoporous framework, without forming agglomerated alumina domains. In these materials, a large fraction of the aluminum presented predominantly tetrahedral oxygen coordination, and only when the Si/Al = 2 ratio was reached, the presence of species in an octahedral environment was evidenced. Most of the aluminum species were well distributed in the mesopores of the Al-incorporated SBA-15 samples, supported by ²⁷Al MAS NMR characterization. Aluminum atoms deposited on the pore walls in the form of hexa-coordinated ions have electron acceptor properties resulting in the generation of Lewis acidic sites. The concentrations of the acid sites estimated from the corresponding Py-FTIR spectra showed a decrease of the C_{Brönsted}/C_{Lewis} ratio with increasing Si/Al molar ratio. However, the mesoporous aluminosilicates that were generated in this study resulted in materials with a large number of Brönsted acid sites, in spite of the high amount of incorporated Al ions evidenced by the results of ²⁷Al MAS NMR characterization. The presence of both tetrahedrally and

octahedrally coordinated aluminum species was substantiated with the tetrahedral ones being more abundant. These results indicated that Al species were mostly incorporated in the SBA-15 structures and the presence of octahedral species was only evidenced in the sample with the lowest Si/Al molar ratio.

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