



# Methods for Pt-WO<sub>3</sub>/SBA-15 materials synthesis for glycerol conversion

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# ABSTRACT

Glycerol has applications as a raw material in different industrial processes, however, its supply exceeds demand. An alternative to increase the added value of this feedstock is its conversion into high added-value chemical products through dehydration and hydrogenation reactions, from which 1,2-PDO and 1,3-PDO can be obtained. To develop catalysts that increase the conversion and selectivity of these processes, materials of 2% Pt and 10% WO<sub>3</sub> supported on SBA-15 were studied. Two methods were used for incipient wetness impregnation: sequential impregnation, with impregnation steps for each species, and co-impregnation, with a single impregnation step for both species. From the analysis of XRD, XRF, N<sub>2</sub> isotherms, SEM, EDS, FTIR, and pyridine FTIR spectroscopy, it was possible to observe the influence of these methods on the structural and textural properties. It was verified that the co-impregnation provided a better dispersion of the WO<sub>3</sub> species on the surface of the SBA-15 and that the reduction process, for both methodologies employed, showed an improvement in the metallic dispersion. The better dispersion of WO<sub>3</sub> species also resulted in a greater formation of Brønsted acid sites for the co-impregnation method, with a predominance of Lewis sites in the structure of the catalysts obtained by both methods.

Keywords: Glycerol; SBA-15; wetness impregnation; mesoporous material.

# **1. INTRODUCTION**

Glycerol is a raw material used in the production of pharmaceuticals, chemicals, cosmetics, and food, and, in 2021, it reached a trade of about 4 million tons and US\$ 2.7 billion [1, 2]. It is the main by-product of the transesterification reaction of fatty acids for the production of biodiesel and is widely available on the market and has a low commercial value (around US\$ 300–500/t in 2021) [3–5]. The transformation of glycerol into new products with higher added value can improve its economy, as well as that of biodiesel. Dehydration of glycerol, followed by hydrogenation (hydrogenolysis), leads to products such as 1,2-PDO and 1,3-PDO with wide application in the market [6]. 1,3-PDO has applications in the production of cosmetics, cleaning products, adhesives, solvents, and resins, and in the pharmaceutical, food, and textile industries, with emphasis on the production of poly(trimethylene terephthalate) (PTT) and polyurethane (PU) [7, 8]. While 1,2-PDO has applications ranging from the pharmaceutical, food, and cosmetic industries, to the manufacture of additives in paints, with emphasis on the production of unsaturated polyester resins [9, 10].

The synthesis of a catalyst for these reactions is a current challenge in materials, as different variables influence the preparation of the support and the active phases that catalyze the reactions of interest. The choice of materials for support synthesis and methods of deposition of metallic phases on the surface is fundamental to obtaining an active and selective catalyst that can be commercially applied in the transformation of glycerol [11, 12]. In the hydrogenolysis reaction, the study of these materials is essential due to the complexity of their mechanism, which involves a series of competitive and sequential reactions, with the desired route depending on the characteristics of the catalyst and the reaction conditions applied in the industrial process (Figure 1). Sequential reactions lead to loss of yield, resulting in unwanted products such as 1-propanol, 2-propanol and propane. In addition, the carboncarbon bonds can be broken, generating ethylene glycol, methanol, ethanol, methane and ethane [13, 14].



Figure 1: Products formed through the dehydration and hydrogenation reaction of glycerol over various catalysts.



Figure 2: Mechanism of dehydration and hydrogenation of glycerol.

Figure 2 presents a schematic diagram of the hydrogenolysis mechanisms to obtain 1,2-PDO and 1,3-PDO. In the production of 1,3-PDO and 1,2-PDO, catalysts containing acidic sites are used for the dehydration of glycerol and metallic sites for the sequential hydrogenation of the intermediate formed in the dehydration. 1,3-PDO is produced when the dehydration of the glycerol molecule occurs from the cleavage of the C-O bond of the secondary carbon, forming the 3-hydroxypropanal (3-HPA) intermediate, which is hydrogenated in the presence of Brønsted sites, available in materials such as Pt/WO<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> [15], Pt/W-MCFs [16], Pt–LiHSiW/ZrO<sub>2</sub> [17], Pt/WO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> [18, 19], Pt/WO<sub>3</sub>/ZrO<sub>2</sub> [20], 2Pt/20(W+Al)-SBA-15 [21], Pt/ZrW<sub>38</sub>Mnx [22], Pt/Nb-WO<sub>x</sub> [23].

In the presence of Lewis acid sites, the cleavage of the C-O bond occurs preferentially at the terminal carbons, leading to the dehydration of glycerol and forming the acetol intermediate, which after the hydrogenation process forms the 1,2-PDO [13, 14]. In the literature, different materials with active phases formed by metallic sites and Lewis sites are used, and examples Ru-WO<sub>3</sub>/ZrO<sub>2</sub> [24], Pt/C [25], Ni/Nb [26], Nb/Pd–Zr–Al [27], Ni/Al-Fe [10]. In some studies, materials with only one metallic phase are also applied to obtain 1,2-PDO, as in the work carried out by AZRI *et al.* [9, 28], in which Cu supported on different materials (dolomite, Al<sub>2</sub>O<sub>3</sub>, bentonite, and montmorillonite) acted both in the dehydration step and in the hydrogenation step.

In hydrogenolysis reactions, the most used supports are  $SiO_2$ ,  $ZrO_2$  and  $Al_2O_3$ . Other materials such as zeolites, clays, and mesoporous materials have also been reported for this use [19, 24, 25]. Silicon-based mesoporous materials, such as SBA-15, present favorable structural characteristics for application as catalyst support, such as high surface area, highly ordered hexagonal channels, thick pore walls, high hydrothermal and mechanical stability, long cycle life, low toxicity and corrosiveness [29–32].

However, SBA-15 has low acidity, so other materials must be added to its structure to improve its catalytic activity, such as organic functional groups, coordination compounds, metallic nanoparticles and metallic oxides [29, 33]. The addition of these materials is facilitated by the high concentration of silanol groups (Si-OH) that promote strong interaction between the support and the ligand and function as active sites for the desired reactions [34]. In the literature, different metals are used in the functionalization of SBA-15, such as Zr and Ru [35], Ni [36], Cu [37], and Fe [38]. The use of various metallic oxides can also be mentioned, such as ZnO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, NiO and MgO [31], WO<sub>3</sub> [21], and TiO<sub>2</sub> [39].

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The addition of metallic species to the surface of SBA-15 can occur at the time of synthesis or after synthesis, however, post-synthetic methods (grafting of reactive metal complexes, adsorption, impregnation, ion exchange, acid treatment, cluster deposition metals, or metallic oxides) have greater advantages, such as obtaining a highly ordered material with higher hydrothermal stability, being increasingly used [34, 40]. The methodology applied in the addition of more than one species can result in catalysts with surface active sites with the necessary interaction to promote the desired reaction at the expense of secondary reactions that decrease the yield of the process. Osakoo *et al.* [41] evaluated the differences between the co-impregnation and sequential impregnation methods in the catalytic activity of the 0.2Pd–10Co-SBA-15 catalyst in the Fischer–Tropsch reaction (FTS) and obtained better results for the sequential impregnation. In another study, Jia *et al.* [42], who used the Pt-Pd/SAPO-41 catalyst in the hydroisomerization reaction of n-hexadecane, observed a higher yield of isohexadecane for the catalysts prepared by co-impregnation when compared to the catalysts in which the sequential methodology was used.

Considering the importance of obtaining a material with a high surface, containing metallic sites with strong hydrogenation properties and specific acid sites (Lewis or Brønsted) for the glycerol transformation reaction, in this work materials containing Pt-WO<sub>3</sub>/SBA-15, (2% wt% Pt and 10% wt% WO<sub>3</sub>), through sequential impregnation of each of the active metals and co-impregnation, in a single step, using a solution containing the two precursor salts. The structural and textural properties of the prepared materials were evaluated to verify the potential of their use as catalysts in glycerol dehydration and hydrogenation reactions.

# 2. MATERIALS AND METHODS

The following reagents were used to synthesize the materials: Pluronic 123 surfactant (P123), tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl), ammonium metatungstate and hexachloroplatinic acid, all from Sigma-Aldrich. Deionized water was used as a solvent in all steps. In the preparation of the materials, pure SBA-15 was first synthesized, followed by the incorporation of platinum and tungsten by sequential incipient co-impregnation and incipient impregnation methods.

# 2.1. SBA-15 synthesis

The first step of the synthesis consisted of mechanically mixing the solution of 140 mL of water, 25 mL of HCl, and 5 g of P123 in a beaker at 40 °C until the surfactant was completely dissolved. Then, 11 mL of TEOS was added and the solution was stirred for 24 h, maintaining heating. At the end of this period, the solution was transferred to a 200 mL autoclave and placed in an oven at 100 °C for 24 h. After the aging period, the material was filtered and washed with ultrapure water until the pH was neutralized. Then, the material was dried at 80 °C for 12 h. Finally, calcination was carried out at 600 °C for 6 h at a heating rate of 2 °C/min, under airflow in a muffle furnace.

# 2.2. Synthesis of Pt-WO<sub>3</sub>/SBA-15 by incipient co-impregnation

Co-impregnation was carried out in a single step incipient impregnation, using a solution of tungsten precursor (ammonium metatungstate) and platinum precursor (hexachloroplatinic acid), containing 10% by mass of WO<sub>3</sub> and 2% by mass of Pt. The method consisted of the dropwise addition of the precursor solution to the SBA-15 material, followed by a 24-hour drying step at 100 °C. Finally, the sample was calcined at 600 °C for 6 h at a rate of 2 °C/min in a muffle furnace. The resulting sample was named Pt-WO<sub>3</sub>/SBA-15 (A).

# 2.3. Synthesis of Pt-WO<sub>3</sub>/SBA-15 by sequential incipient impregnation

The sequential impregnation occurred in two stages of incipient impregnation: the first using tungsten precursor solution and the second using platinum precursor solution, with the same concentrations of the co-impregnation step. The first impregnation followed the same methodology described above - addition of the ammonium metatungstate solution, drying in an oven at 100 °C for 24 hours, and calcination at 600 °C for 6 h (2 °C/min). Then, the sample (WO<sub>3</sub>/SBA-15) was impregnated with the precursor solution of Pt, following the same procedure. The co-impregnation and sequential impregnation materials were named Pt-WO<sub>3</sub>/SBA-15 (A) and Pt-WO<sub>3</sub>/SBA-15 (B), respectively. All materials synthesized and impregnated with Pt were reduced at a temperature of 350 °C for 2 h, under H<sub>2</sub> flow (100 mL/min), to obtain the metallic phase. The materials resulting from this process were named Pt-WO<sub>3</sub>/SBA-15 (B-R).

#### 2.4. Materials characterization

The characterization by X-ray diffraction (XRD) was performed in a Bruder D2 Phaser diffractometer, equipped with a Lynxeye detector, using CuK $\alpha$  radiation ( $\lambda = 1.54$  Å), Ni filter, divergent slit of 0.1 nm, current of 10 mA

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and voltage of 30 kV. The analyzes were conducted at a low angle  $(0.8^\circ \le 2\theta \le 5^\circ)$ , at a step of 0.01°, and high angle  $(x^\circ \le 2\theta \le y^\circ)$  at a step of 0.02°. The average particle size was calculated using the Scherrer equation:

$$T_c = \frac{\lambda k}{FWHM(rad) * \cos\theta(rad)}$$
(1)

where FWHM is the full width of the peak, " $\theta$ " is the scattering angle in radians, " $\lambda$ " is the wavelength, and "k" is the Scherrer constant that takes on values between 0.89 and 0.94, depending on the shape of the crystallite. This work used the approximation for spherical-shaped particles (k = 0.89) [41].

The Fourier Transform Infrared (FTIR) spectra were obtained using Shimadzu Prestige 21 IR Spectrophotometer equipment. The samples were analyzed in the form of spectroscopic grade potassium bromide pellets (KBr) in the spectral range of 4000–450 cm<sup>-1</sup>.

Scanning Electron Microscopy (SEM) on a Tescan VEGA 3 LMU instrument and composition analysis from energy dispersion X-ray spectroscopy (EDS) on an Oxford Instrument X-act model 51-ADD0007 equipment.

Raman spectroscopy was performed on a LabRam Evolution equipment with a CCD detector at room temperature. The 532 nm laser edge was used as an exciting source with a power of 100 mW.

The textural properties were determined by physisorption of  $N_2$  at -196 °C using the Quantachrome equipment model Nova 2200. The samples were pre-treated under vacuum, taking them from room temperature to 100 °C and remaining there for 15 min, followed by heating to 200 °C, remaining at this temperature for 15 min, and heating to 350 °C, remaining at this temperature for 30 min. The surface area and pore distribution were determined by the Brunauer-Emmet-Teller (BET), and Barrett-Joyner-Halenda (BJH) methods respectively. To determine the microporosity of the materials, the t-plot method was used.

Pyridine FTIR spectra were obtained on a Nicolet 5700 spectrometer with an optical resolution of 2 cm<sup>-1</sup> in the spectral range of 1400–1800 cm<sup>-1</sup>. The materials were pressed in the sample holder and mounted in the spectrometer cavity, and then pre-treated at 20 to 450 °C under dry air flow (100 cm<sup>3</sup> min<sup>-1</sup>) overnight. Then the samples were degassed (10<sup>-5</sup> bar) for 1 h at 200 °C. For the adsorption of pyridine, the probe was adsorbed at 150 °C, around 1 to 2 mBar for 5 minutes, and the physisorbed pyridine was removed using a vacuum for 1 h. The IR spectra were obtained for temperatures 150 and 250 °C at gradual heating.

## 3. RESULTS

#### 3.1. X-ray powder diffraction (XRD) patterns

The low-angle XRD pattern of SBA-15 (Figure 3), showed three peaks around  $2\theta = 0.9^{\circ}$ , 1.65° and 1.90°. These are attributed to the crystallographic planes of SBA-15 in the Miller indices (100), (110), and (200), which prove the formation of the ordered mesoporous structure with hexagonal symmetry [43–45]. The same pattern is observed in all materials (reduced and non-reduced), prepared by both the co-impregnation methods (A) and the sequential impregnation method (B). It can be inferred that the support structure is preserved after the different processes and stages of material preparation.

The wide-angle XRD patterns of the materials showed similar profiles (Figure 4). A shoulder peak between 20 and 25° was observed in the SBA-15 diffractogram, corresponding to the amorphous structure of silica [29, 36]. For the other samples, it was possible to evaluate the formation and presence of oxide and metallic species in the materials after the calcination process and, before and after the reduction. Diffraction peaks at  $2\theta = 23.1^\circ$ ,  $23.6^\circ$ ,  $24.4^\circ$ ,  $26.5^\circ$ ,  $28.8^\circ$ ,  $33.3^\circ$ ,  $41.6^\circ$ ,  $49.9^\circ$ , and  $55.9^\circ$  were observed, mainly before the reduction process, which are indexed to the presence of monoclinic species of WO<sub>3</sub> (ICSD: 084843). It was also observed that the diffractogram of the Pt-WO<sub>3</sub>/SBA-15 material (A) showed low-intensity peaks referring to the WO<sub>3</sub> species when compared to the material prepared by sequential impregnation (Pt-WO<sub>3</sub>/SBA-15 (B)). These low-intensity peaks can be attributed to a greater dispersion of WO<sub>3</sub> on the surface of SBA-15 incorporated by co-impregnation than by sequential impregnation, as discussed by ÁLVAREZ *et al.* [46] studying the dispersion of WO<sub>3</sub> on the surface of the catalyst Al/SBA-15.

The particle size of WO<sub>3</sub> was calculated using the Scherrer equation. The calculated size in the Pt-WO<sub>3</sub>/SBA-15 material (A) was 8.68 nm and in the Pt-WO<sub>3</sub>/SBA-15 sample (B) it was 16.94 nm. The best dispersion of WO<sub>3</sub> was obtained in the Pt-WO<sub>3</sub>/SBA-15 material (A). After sample reduction, the peaks attributed to the presence of monoclinic species of WO<sub>3</sub> showed a decrease in intensity. However, it is observed that this behavior is intensified in the Pt-WO<sub>3</sub>/SBA-15 (A-R) sample. It is observed that samples prepared by co-impregnation were more sensitive to heat treatments than samples prepared by sequential impregnation. This behavior is attributed to an increase in the interaction of WO<sub>3</sub> particles with SBA-15 with a decrease in particle size and



**Figure 3:** X-ray powder diffraction patterns of materials and precursors at  $2\theta$  in the range between 0.8 and 5°: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (B) and Pt-WO<sub>3</sub>/SBA-15 (B).



**Figure 4:** X-ray powder diffraction patterns of materials and precursors at 20 in the range between 20° and 80°: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (B) and Pt-WO<sub>3</sub>/SBA-15 (B).

an increase in dispersion [46, 47]. The co-impregnation method promoted an increase in the dispersion of  $WO_3$  particles, favoring a better resistance to the thermal treatments of the materials.

In the unreduced Pt-WO<sub>3</sub>/SBA-15 (A) and (B) materials, four diffraction peaks corresponding to platinum in its oxide form (ICSD 030444) were observed:  $2\theta = 34.2^{\circ}$ ,  $39.7^{\circ}$ ,  $46.2^{\circ}$  and  $67.5^{\circ}$  (Figure 4). After the reduction, only the peaks located at  $2\theta = 39.8^{\circ}$ ,  $46.3^{\circ}$ ,  $67.5^{\circ}$  were observed. These peaks were attributed to platinum in its metallic form (ICSD 064917) (Pt-WO<sub>3</sub>/SBA-15 (A-R) and (B-R) materials). The peaks of the PtO<sub>2</sub> species, previously located at  $2\theta = 34.2^{\circ}$  and  $39.7^{\circ}$ , were not observed in these samples, proving the effectiveness of the reduction process. The other peaks referring to platinum in its oxide form were overlapped with metallic phase.



**Figure 5:** FTIR spectra of materials in the wavelength range 450–4000 cm<sup>-1</sup>: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (B) and Pt-WO<sub>3</sub>/SBA-15 (B-R).

The size of the metallic platinum particles in the Pt-WO<sub>3</sub>/SBA-15 (A-R) and (B-R) materials was calculated using the Scherrer equation. For the Pt-WO<sub>3</sub>/SBA-15 (A-R) sample synthesized by co-impregnation, the platinum crystallite size was 42 nm, while for the Pt-WO<sub>3</sub>/SBA-15 (B-R) sample by sequential impregnation it was 28 nm. ZHU *et al.* [48] studied the dispersive effect and sizes of Pt particles supported on SBA-15, the size of the platinum crystallite is related to its dispersion on the SBA-15 surface. Thus, it can be attributed that the sequential impregnation method under the conditions studied favored the formation of smaller platinum particles on the surface of SBA-15, promoting a better metallic dispersion of the platinum species.

## 3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The prepared materials were characterized by infrared spectrometry (FTIR) to identify the vibrational frequencies referring to the functional groups of the structure (Figure 5). The bands at 3354 cm<sup>-1</sup>, present in all spectra, are attributed to the vibrations of axial deformation of the internal and external hydroxyl groups (–OH) in the mesoporous structure, while the absorption bands at 1631 cm<sup>-1</sup> refer to vibrations of angular deformation of free water molecules adsorbed on the surface of materials [29, 31, 49]. In the unmodified SBA-15, it is possible to identify the band at 962 cm<sup>-1</sup>, characteristic of the asymmetric vibrations of the Si-OH bonds generated by the presence of defective sites in the structure, while in the spectrum of Pt-WO<sub>3</sub>/SBA-15 materials this band shows a slight reduction, confirming the interaction between the Si-OH and W groups and the formation of Si-O-W bonds in the material [29].

The band at 1054 cm<sup>-1</sup> is attributed to the asymmetric deformation modes of the Si-O-Si bonds. With the addition of W, there was a decrease in this band, indicating the formation of Si-O-W bonds. The other bands, at 800 cm<sup>-1</sup> and 437 cm<sup>-1</sup>, refer to the vibrations of asymmetric deformations of the Si-O bonds and the vibrations of angular deformation of the Si-O bonds at the tetrahedral sites, respectively [31]. In the samples, bands referring to the vibrations of the organic molecules of P123 were not observed, which are usually found at 2960–2870 cm<sup>-1</sup>, related to the stretching between the C-H bond of the CH<sub>2</sub> groups. In addition, no bands referring to the deformations of the  $-(CH_2)_n$  bond, around 1460 cm<sup>-1</sup>, and no deformations of the C-O-C bond of P123 were observed, in the band region of 1380 cm<sup>-1</sup>, which reassures that the driver agent removal method was effective [31, 50].

#### 3.3. Scanning Electron Microscope (SEM)

The SEM images and elemental mapping (MAP) of the materials are shown in Figures 6 and 7. SBA-15 showed the morphology of uniform cylindrical stems (Figure 6a). After the addition of  $WO_3$  and Pt, and the calcination and reduction of the materials, a granular pattern with less particle aggregation was observed (Figure 6b-c) in the



Figure 6: SEM images: a) SBA-15 b) Pt-WO<sub>3</sub>/SBA-15 (A-R) c) Pt-WO<sub>3</sub>/SBA-15 (B-R).



Figure 7: Mapping of the composition of materials by EDS. A) Pt- WO<sub>3</sub>/SBA-15 (A-R) B) Pt-WO<sub>3</sub>/SBA-15 (B-R).

morphology of SBA-15. Furthermore, it was possible to observe that the Pt-WO<sub>3</sub>/SBA-15 materials presented a more heterogeneous particle size profile when compared to the SBA-15 sample [29, 51]. The different morphologies that this material presents are related to the synthesis conditions applied (temperature, pH of the solution, calcination steps, modification agents used, among others) and will influence the diffusion of molecules in their pores and their ability to absorb [43, 52–54].

From the mapping of Pt and W metals presented in Figure 7, it is possible to observe that the metallic particles are dispersed on the surface of the Pt-WO<sub>3</sub>/SBA-15 materials synthesized both by co-impregnation (A) and by sequential impregnation (B). In the W mapping images, it is possible to observe more points or brighter points in some areas, indicating a greater amount of metal.

### 3.4. RAMAN spectroscopy

The study by Raman spectroscopy allowed the analysis of the different species of tungsten presented in the synthesized materials. The results referring to this analysis are presented in Figure 8 and the attributions for the bands are presented in Table 1. In all materials, Raman scattering bands located around 260–270 cm<sup>-1</sup>,  $328 \text{ cm}^{-1}$ ,  $713-716 \text{ cm}^{-1}$ ,  $798-804 \text{ cm}^{-1}$  were observed. The presence of bands  $713-716 \text{ cm}^{-1}$  and  $798-804 \text{ cm}^{-1}$  indicate that there are crystalline WO<sub>3</sub> nanoparticles in all materials. When comparing the spectra of the materials synthesized by co-impregnation and sequential impregnation, it is possible to observe that the samples by co-impregnation present a larger number of waves, suggesting a stronger interaction between WO<sub>3</sub> and the support, and smaller WO<sub>3</sub> species, consistent with what was observed in XRD analysis. Since smaller particles indicate a greater dispersion on the material's surface, it is suggested that the co-impregnation has more dispersed WO<sub>3</sub> species [18, 56].

In the materials prepared by both methodologies, a lower intensity of the bands was observed after the reduction process, which suggests a better dispersion of  $WO_3$  on the surface of the support and a smaller amount of crystalline  $WO_3$  nanoparticles and shows that this process interferes with the interaction between the impregnated species and the support [18, 56]. A new band was also observed in the reduced Pt/WO<sub>3</sub>/SBA-15 (B) catalyst located at 377 cm<sup>-1</sup>, which is attributed to the bending modes of the O-W-O bonds.

# 3.5. Textural analysis of nitrogen adsorption/desorption isotherms

The nitrogen adsorption/desorption isotherms of the materials are shown in Figure 9 and the estimated texture parameters are presented in Table 2. All materials showed micro and mesopores. The nitrogen adsorption/ desorption isotherms showed a type IV profile and type I hysteresis, with capillary condensation at average relative pressures corresponding to the ordered mesoporous structure of the SBA-15 support (Figure 9). It is also



**Figure 8:** Raman spectra of the materials: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A), Pt-WO<sub>3</sub>/SBA-15 (A-R), Pt-WO<sub>3</sub>/SBA-15 (B) and Pt-WO<sub>3</sub>/SBA-15 (B-R).

Table 1: Raman frequencies of the Pt-WO<sub>3</sub>/SBA-15 (Ref. LEE and WACHS [55], LIANG et al. [18]).

WAVELENGTH (cm <sup>-1</sup> )	ASSIGNMENTS	
260–270	Deformation modes of W-O-W bonds of the octahedral $WO_x$	
328	Tetrahedral tungstate species	
377	O-W-O bending modes	
713–716	Stretch modes of the W-O-W bond of the octahedral $WO_x$	
798-804	Bending modes of the W-O-W bonds of the octahedral $WO_x$	



**Figure 9:**  $N_2$  adsorption/desorption isotherms of the materials: a) SBA-15 b) Pt-WO<sub>3</sub>/SBA-15 (A) c) Pt-WO<sub>3</sub>/SBA-15 (A-R) d) Pt-WO<sub>3</sub>/SBA-15 (B) e) Pt-WO<sub>3</sub>/SBA-15 (B-R).

observed in all prepared materials at low relative pressures up to about 0.1, the presence of micropores in the materials [45, 57]. Smaller hysteresis loops were also observed for the post-impregnation and reduction materials. It can be inferred a partial occupation of the mesopores of the materials by the tungsten oxide species [41].

The surface area of the SBA-15 support was 756  $m^2g^{-1}$  (Table 2), which is consistent with the literature for this material, which is between 633–758  $m^2g^{-1}$  [29, 31, 41, 57]. After the incorporation of the metals, a

MATERIAL	S BET <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	D <sub>PORE</sub> (nm)	$\frac{V_{\text{TOTAL}}^{b}}{(cm^{3}g^{-1})}$	$V_{\text{micropore}}^{c}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{MESOPORE}}^{c}$ (cm <sup>3</sup> g <sup>-1</sup> )
SBA-15	756	5.9	1.05	0.03	1.02
Pt-WO <sub>3</sub> /SBA-15 (A)	532	5.5	0.73	0.02	0.71
Pt-WO <sub>3</sub> /SBA-15 (A-R)	531	5.6	0.75	0.02	0.73
Pt-WO <sub>3</sub> /SBA-15 (B)	494	5.2	0.65	0.01	0.64
Pt-WO <sub>3</sub> /SBA-15 (B-R)	495	5.6	0.73	0.01	0.72

Table 2: Textural properties of synthesized SBA-15 type materials.

 $^{a}$ Calculated by BET method;  $^{b}$ Calculated by BJH method;  $^{c}$ Calculated by t-plot method;  $^{d}V_{mesopore} = V_{total} - V_{micropore}$ 



Figure 10: Mesopores size distribution graph.

decrease in the surface area, diameter, and volume of micro and mesopores was observed, which may be due to the aggregation of these particles on the surface or inside the channels [31].

The sample synthesized by co-impregnation, Pt-WO<sub>3</sub>/SBA-15 (A) had a higher surface area ( $532 \text{ m}^2\text{g}^{-1}$ ) and pore volume (0.73 cm<sup>3</sup>g<sup>-1</sup>) when compared to the Pt-WO<sub>3</sub>/SBA-15 sample (B), with a surface area of 494 cm<sup>3</sup>g<sup>-1</sup> and a pore volume of 0.65 cm<sup>3</sup>g<sup>-1</sup>. These results suggest that the sequential impregnation method showed a lower blockage of the support pores due to the smaller particle size and better distribution of the oxide species on the surface of SBA-15, in agreement with the XRD and Raman analyses. The surface areas of the materials before and after reduction were similar for each material, with an increase only in the total volume of pores and in the diameter of pores in the post-reduction materials, a behavior intensified in the sample by sequential impregnation.

The mesopore size distribution graph of the materials is shown in Figure 10. It is possible to observe the greater volume and diameter of mesopores of the material SBA-15, while the other samples showed lower values for these parameters. All  $Pt-WO_3/SBA-15$  materials showed a uniform mesopore size range, with similar pore volume and diameter values.

An important analysis of the distribution of Pt and  $WO_3$  particles in the synthesized materials can be carried out in view of the values found for the size of the Pt crystallite and of the  $WO_3$  species through the XRD results and the pore size distribution of the SBA-15. The particle size found for Pt was 28 nm and 42 nm and for the  $WO_3$  particles of 8.68 nm and 16.94 nm, for the co-impregnation and sequential impregnation methods, respectively, and the pore size of SBA-15 in both methods is well below this value (about 5 nm). Thus, it is possible to state that these particles are found on the surface of the material, and not in its pores. According to ZHU *et al.* [48], this finding is important from the catalytic point of view because the size of these particles and their distribution influence their catalytic performance.

## 3.6. Pyridine FTIR spectroscopy

The FTIR spectra of pyridine chemisorbed on the materials are shown in Figure 11. The main bands observed in the spectra were at 1637, 1615, 1543, 1490, and 1453 cm<sup>-1</sup>, attributed to vibrational modes 8a, 8b, 19a and 19b of the adsorbed pyridine. The Brønsted acid sites have peaks at 1637, 1543, and 1490 cm<sup>-1</sup>, and the Lewis sites at 1615, 1490, and 1453 cm<sup>-1</sup> [58]. The relative intensity of the bands at 1545 and 1450 cm<sup>-1</sup>, referring to pyridine adsorbed on acidic sites of Brønsted and Lewis (Table 2), was evaluated for studies on the change in the nature of the sites.

For the SBA-15 support, the presence of acidic sites was not observed under the conditions studied. However, when  $WO_3$  and Pt were added to the surface of SBA-15, bands attributed to the formation of Lewis acid sites in the materials were observed, regardless of the preparation method in the temperature range of 150 °C.



**Figure 11:** Pyridine FTIR spectra of prepared materials: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A-R) and Pt-WO<sub>3</sub>/SBA-15 (B-R). (Single column fitting and color should be used).

With the system's temperature increase, a reduction in these bands is observed, suggesting that these sites are weak and moderate-intensity (Table 3) [59]. According to GONZÁLEZ *et al.* [60], Lewis sites on the surface of Pt-WO<sub>3</sub>/SBA-15 materials are due to the presence of oxygen defects in the crystalline structure of WO<sub>3</sub>.

In the synthesized materials, a small amount of Brønsted sites was observed, which may be related to the presence of WO<sub>3</sub> species in the crystalline phase and poorly dispersed on the material's surface. The generation of Brønsted acid sites in the SBA-15 structure is linked to the good dispersion of these species that allows their interaction with the hydroxyl groups of silanols [47, 61]. In the study by ZHU *et al.* [47] it was observed that for concentrations of up to 10% of WO<sub>3</sub>, supported on Al<sub>2</sub>O<sub>3</sub>, there was no formation of crystalline structures on the surface of the material. However, with the increase of this content, there was a formation of crystalline WO<sub>3</sub> species and a reduction of acidity from Brønsted. Other authors have also studied the relationship between the dispersion of oxide species on the surface of the material and the formation of Brønsted sites, such as the work carried out by MUTLU and YILMAZ [62], in which the increase in the percentage of WO<sub>3</sub> resulted in a lower dispersion of these species on the surface of the WO<sub>3</sub>/Zr-SBA-15 catalyst and a smaller number of acidic sites.

The small amount of Brønsted acid sites generated in the material may also be linked to the applied calcination temperature, which may have promoted the greater formation of the monoclinic  $WO_3$  structure at the expense of its hexagonal shape, as observed by HUNYADI *et al.* [63], when studying the influence of temperature on the decomposition of ammonium metatungstate, under a synthetic air atmosphere. Moreover, it was possible to establish a relationship between the impregnation method used and the number of acid sites in

MATERIAL	BRØNSTED ACIDITY (µmol.g <sup>-1</sup> )	LEWIS ACIDITY (µmol.g <sup>-1</sup> )
SBA-15 (150 °C)	0	0
SBA-15 (250 °C)		
Pt-WO <sub>3</sub> /SBA-15 (A) (150 °C)	11.42	91.63
Pt-WO <sub>3</sub> /SBA-15 (A) (250 °C)	0	14.18
Pt-WO <sub>3</sub> /SBA-15 (B) (150 °C)	6.83	93.65
Pt-WO <sub>3</sub> /SBA-15 (B) (250 °C)	0	10.11

**Table 3:** Number of acid sites of the synthesized materials: SBA-15, Pt-WO<sub>3</sub>/SBA-15 (A-R) and Pt-WO<sub>3</sub>/SBA-15 (B-R) at the analysis temperatures of 150 and 250  $^{\circ}$ C.

the material, in which the co-impregnation methodology promoted more dispersed  $WO_3$  particles, resulting in a higher Brønsted acidity for these materials when compared to those obtained by sequential impregnation [62].

Another factor that influences the acidity is the size and dispersion of the Pt particles. According to LEI *et al.* [64], using the catalyst Pt-WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, the agglomeration of Pt particles reduces the interfacial sites between Pt and WO<sub>x</sub>, which results in a decrease in the number of Bronsted sites. In the study carried out by ZHU *et al.* [47], in which the catalyst was used, it was possible to observe that the larger the size of the Pt crystallite, lower was the activity of the catalysts and their acidity, due to the formation of agglomerates and blockage of pores. The size of the Pt particles found in the present work are larger than those obtained for catalysts with the same active phase in the literature, as in the cited studies, and this may also be a justification for the small number of acid sites obtained for the Pt-WO<sub>3</sub>/SBA-15 materials.

Different studies that applied catalysts supported on siliceous materials showed good activity in hydrogenolysis reactions. NIU *et al.* [65] studying Pt/WO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts obtained 72.5% conversion and 39.2% selectivity for 1,3-PDO. FENG *et al.* [19], with Pt/WO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> type catalysts promoted a 48% conversion of glycerol and 56% selectivity for 1,3-PDO. In a later study, these same authors [66] tested this same active phase supported on mesoporous silica (Pt/WO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SBA-15) under similar reaction conditions, observing a conversion of 60% of glycerol and a selectivity of 50% for 1,3-PDO, and consequently a higher yield with the use of SBA-15.

The promising use of SBA-15 was also observed in the study by FAN *et al.* [67], with Pt-WO<sub>3</sub>/SBA-15 catalyst. These authors obtained 86% of glycerol conversion and 70% of selectivity for 1,3-PDO, using a longer reaction time compared to the other articles. In the mentioned studies, the acidity observed in these materials was higher than that obtained in the present work, however, analyzing the physicochemical characteristics of the catalysts obtained, it is possible to state that adjustments in synthesis conditions such as the calcination temperature and a higher dispersion of metallic particles would promote greater acidity in Pt-WO<sub>3</sub>/SBA-15 catalysts.

# 4. CONCLUSIONS

The synthesis method of the applied SBA-15 material resulted in the formation of an ordered and stable hexagonal mesoporous structure that was not affected by the heat treatment after sequential impregnation or coimpregnation with WO<sub>3</sub> and Pt. The insertion of WO<sub>3</sub> into SBA-15 allowed the formation of Lewis and Brønsted acid sites. The co-impregnation method resulted in better structural properties, a greater number of acidic sites, and a greater distribution of WO<sub>3</sub> species, with a predominance of Lewis sites on the surface of the SBA-15 material. The prepared Pt-WO<sub>3</sub>/SBA-15 material can be used as the bifunctional catalyst, with metallic sites and acid sites, with favorable characteristics for application in dehydration and hydrogenation reactions of the glycerol molecule.

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