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# Catalytic conversion of glucose into sorbitol over niobium oxide supported Ru catalysts

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Keywords: Ruthenium Niobium oxide Hydrogenation Glucose Sorbitol	Sorbitol is a sugar alcohol of great importance in cosmetic, food and pharmaceutical industry as well as the production of biopolymers. This work aimed at the synthesis of sorbitol from the hydrogenation of glucose using Ru/Nb <sub>2</sub> O <sub>5</sub> catalysts in the amorphous and crystalline phases. The catalysts were synthesized from the wet impregnation method and characterized by N <sub>2</sub> adsorption isotherms, TGA/DTG, EDXRF, XRD, TPR-H <sub>2</sub> , XPS and SEM. The catalytic tests presented results of high conversion rates of glucose reaching 85 % and 99 % of selectivity to sorbitol when using Nb <sub>2</sub> O <sub>5</sub> in the crystalline form as support, and 53 % and 55 % in the conversion and selectivity, respectively, when the amorphous phase of Nb <sub>2</sub> O <sub>5</sub> was used as support. The structural modification of the catalytic support positively favored the catalyst activity and sorbitol production, allowing the formation of nanometric particles of the active metal on the surface alongside the increase of the mesoporosity,			

thereby facilitating the transport of reagents.

### 1. Introduction

Sorbitol, a sugar alcohol formed by six carbons and six hydroxyl groups in its structural formula, stands out as a high value-added polyol used as an additive in food, pharmaceutical and cosmetic industries. Its main applications are as sweetener, humectant, dispersant, excipient, thickener, mainly in the production of sugar-free products, and vitamin C, which constitute about 24 % and 15 % of the total application market, respectively [1,2]. Other applications of this polyol are in the production of liquid alkanes, glycols, isosorbide, which, like sorbitol itself, are also important monomers in the production of various types of polymers (polyurethane, polycarbonate, absorbents and biocomposites) [3–7].

The establishment of sorbitol as a platform and alternative molecule in the production of chemical derivatives by the US Department of Energy (DOE) in 2004 further evidenced the possibility of obtaining this product not only from the hydrogenation of corn syrup, but also from lignocellulosic feedstocks [1,8,9].

Despite being found naturally in fruits, sorbitol can be produced synthetically by the catalytic hydrogenation of glucose, biotechnological processes, and electroreduction of glucose. The catalytic hydrogenation of glucose process is the most industrially used due to the easiness in the production and processing steps of the product, requiring the use of mild temperatures and high pressures [10,11]. Nickel-based catalysts, such as Raney-Ni, have been extensively used for this type of reaction due to their low cost. This catalyst has as downsides the (1) deactivation and leaching of nickel species into the reaction solution, forming chelates, requiring their withdrawals in purification steps and (2) catalyst replacement [12–15].

As an alternative to the use of nickel, the development of catalysts using noble metals such as ruthenium has advantages in thermal and mechanical stability, and the ability to maintain the same catalytic activity after long-term cyclability. Despite their higher cost, these have been very effective for higher conversion and selectivity of the carbonyl group in alcohol [16–18]. The use of different catalyst supports may result in new properties to the catalyst, such as structural and morphological characteristics and, mainly, in the catalytic performance in activity and selectivity to the product of interest, with further production costs [2,19,20]. Catalyst supports such as activated carbon and carbon have shown long-term chemical and mechanical stability in different reaction conditions and prone to modification of surface area

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and physical properties, aiming at improving the pore size and electronic structure [21-23]. Other types of supports are amorphous alloys, zeolites and ordered mesoporous silicas (MCM), which allowed a better diffusion of glucose molecules, better metallic dispersions and the use of lower pressure reaction conditions, resulting in advances in the synthesis of materials and higher selectivity and conversion [19,24-27].

The use of oxides as supports for more active metals than nickel allows the reduction of costs with pre and post-reaction steps, longer recycling times with the use of more stable materials, without the loss of material to the reaction solution by leaching. Oxide supports appear as an option, since they have exceptional durability during the process of hydrogenation of glucose, favoring the reaction with the adsorption of hydrogen on its surface, thereby favoring the reaction [28]. Other reactions also use oxide catalyst supports and involve the transformation of glucose such as the oxidation of glucose to gluconic acid in gold catalysts supported on  $Al_2O_3$ ,  $CeO_2$  and  $ZrO_2$  [29]; and dehydration of glucose to 5-HMF, using  $Al_2O_3$ -B<sub>2</sub>O<sub>3</sub> [30].

Maris et al. [31] evaluated the use of the Ru/SiO<sub>2</sub> catalyst in the hydrogenation of glucose and observed that due to the inert nature of the support, there was a minimization of the formation of by-products, obtaining 100 % selectivity to sorbitol. However, the increase in the particle size of the active metal through sintering, had a negative impact on the reaction rate, obtaining lower glucose conversions. Mishra et al. [32] reported the use of mixed oxides of TiO<sub>2</sub>/NiO, obtaining an increase in selectivity (92.6–96.6 %) to sorbitol when compared to TiO<sub>2</sub> supports. The difficulties presented by oxide supports occurred due to the formation of agglomerates with the growth of the size of the Ru particle in long reaction times. Moreover, the poisoning by adsorption of reaction by-products negatively affected the catalytic activity of the material, the mechanical stability and the yield to sorbitol.

The different structural and chemical properties presented by niobium oxide, such as the support effect, in which there is a strong metallic interaction with the active phase (SMSI - strong metal-support interaction), polymorphism and promoter effect; may cause variations in yields to reaction products and catalytic activity, ensuring its applications in numerous types of reactions [33–40].

The use of thermal processes in the generation of crystalline forms of niobium oxide and application as support in Fischer-Tropsch reaction resulted in different catalytic activities and selectivities. For crystalline niobia, despite the decrease in specific surface area and pore volume after heat treatment, a selectivity of 70 % for  $C_{5+}$  was achieved, whereas when using amorphous niobia only 49 % was obtained [41].

Regarding the use of Nb<sub>2</sub>O<sub>5</sub> in sugar processing, the use of niobium oxide in the amorphous form to produce furfural from the dehydration of xylose using a water/toluene medium, proved to be determinant as the most active (93 % conversion) and selective (48 %) catalyst for the reaction. The presence of Lewis acid sites in its structure, easy separation of the catalyst and high reusability showed as essential for these results when compared to homogeneous catalysts (HCl and Sc(OTf)<sub>3</sub>) [42]. Kreissl et al. [43] evaluated the correlation between the tunable acidity quantity and strength of niobium oxides and their morphologies as well as their application in sucrose transformation to 5-HMF. The authors noticed that the presence of both acid types and variation of strength lead to different 5-HMF yield. Furthermore, for the conversion of sucrose, glucose and fructose components, the mesoporous niobium oxide presented the highest HMF yield (36 % for each sugar) due to the balanced quantity of Brønsted and Lewis acid sites and strengths. Luo et al. [44] carried out a study of the application of Nb<sub>2</sub>O<sub>5</sub> as a support alternative for Ru in the hydrogenation of levulinic acid at 473 K and 40 bar of H<sub>2</sub>. The use of Nb<sub>2</sub>O<sub>5</sub> promoted a 61.8 % yield in the formation of  $\gamma$ -valerolactone (GVL) and low selectivity to other reaction products such as methyltetrahydrofuran (MTHF). It was also noted that there was excellent stability of the material with low leaching rates of Ru for the reaction medium (maximum of 2%).

Therefore, the present work aimed at the synthesis, characterization and evaluation of ruthenium catalysts supported on niobium oxide in amorphous and crystalline phases in the hydrogenation of glucose to sorbitol.

# 2. Experimental section

## 2.1. Catalyst synthesis

The preparation of ruthenium catalysts supported on niobium oxide was carried out by the wet impregnation method with 5 wt% Ru, using ruthenium(III) chloride salt (RuCl<sub>3</sub>.xH<sub>2</sub>O, Sigma Aldrich, 45–55 wt% Ru) as a metal precursor and hydrated niobium oxide (Nb<sub>2</sub>O<sub>5</sub>.xH<sub>2</sub>O, HY-340, CBMM – Companhia Brasileira de Metalurgia e Mineração), as support.

Firstly, the pretreatment of the support at 393 K for 6 h in a muffle furnace was carried out to remove moisture and contaminants (Nb<sub>2</sub>O<sub>5</sub> in amorphous phase (Nb<sub>2</sub>O<sub>5</sub>\_A)). Then, a part of the pre-treated oxide was subjected to heat treatment for 4 h at 873 K, also in a muffle furnace to obtain the crystalline phase of Nb<sub>2</sub>O<sub>5</sub> (Nb<sub>2</sub>O<sub>5</sub>\_C). Separately, the resulting oxides were placed in evaporation flasks together with aliquots for the required ruthenium content, under agitation for 24 h, with subsequent drying at 343 K using a vacuum pump.

After drying, the prepared samples were calcined in a muffle for 4 h at 673 K with a heating rate of 10 K min<sup>-1</sup>, in order to reduce the content of precursor salt in the synthesized samples and formation of ruthenium oxide. The synthesized samples were named as indicated in Table 1:

The catalysts were stored under ambient conditions for subsequent catalytic reduction and hydrogenation.

# 2.2. Catalyst characterization

The catalysts, as well as the supports, were characterized by different techniques.

The TG/DTA curves were obtained using a DTG-60 Shimadzu equipment in the temperature range of 298-1073 K at a rate of 10 K min<sup>-1</sup> and conducted under inert air atmosphere using a mass of approximately 3 mg of the sample.

X-ray powder diffraction (XRD) patterns of the synthesized catalysts were performed in a Shimadzu XRD 6100 X-ray diffractometer with  $CuK_{\alpha}$  tube operating at 40 kV and 30 mA. Firstly, the materials were analyzed in the range of  $2\theta = 10-80^{\circ}$  and a scanning rate of  $2^{\circ}$  min<sup>-1</sup> to obtain the crystallographic profile of the samples. Then, the crystalline samples were scanned again in the range of  $26^{\circ}$  and  $38^{\circ}$  with scanning rate  $0.25^{\circ}$  min<sup>-1</sup> for better identification of the peaks indexed to RuO<sub>2</sub> and calculation of the crystallite size from the Scherrer equation (Eq. 1):

$$d_{hkl} = \frac{K\lambda}{\beta_{1/2}\cos\theta}$$
(1)

where  $d_{hkl}$  is the mean diameter of the crystallite size (nm),  $\lambda$  is the cell wavelength used by the XRD equipment (0.1541 nm), K is the Scherrer constant, related to the shape of the crystallite (for spherical shaped particles, value equal to 0.89),  $\beta_{1/2}$  is the corrected peak width for the spread of the equipment in radians (in radians),  $\cos\theta$  is the cosine of the angle of the refractive peak.

The determination of the particle size related to  $Ru^0$ , the following correlation was used (Eq. 2):

Table 1Nomenclature of prepared samples.

SAMPLE NAME	CATALYST
Nb <sub>2</sub> O <sub>5</sub> _A	Nb <sub>2</sub> O <sub>5</sub> in amorphous phase
Nb <sub>2</sub> O <sub>5</sub> _C	Nb <sub>2</sub> O <sub>5</sub> in crystalline phase
5RuNb <sub>2</sub> O <sub>5</sub> _A	5% Ru/Nb <sub>2</sub> O <sub>5</sub> in amorphous phase
5RuNb <sub>2</sub> O <sub>5</sub> _C	5% Ru/Nb <sub>2</sub> O <sub>5</sub> in crystalline phase

$$d_{Ru^{0}} = \sqrt[3]{\frac{MA_{Ru}}{MM_{RuO_{2}}}} \frac{\rho_{RuO_{2}}}{\rho_{Ru}} \cdot d_{RuO_{2}}$$
(2)

where  $d_{Ru}^{\circ}$  is the diameter of the ruthenium particle (nm), MA<sub>Ru</sub> is the atomic mass of ruthenium (101.07 g mol<sup>-1</sup>),  $MM_{RuO_2}$  is the molecular mass of ruthenium oxide (133.07 g mol<sup>-1</sup>),  $\rho_{Ru}$  is the density of ruthenium metal (12.1 g.cm<sup>-3</sup>),  $\rho_{RuO_2}$  is the density of ruthenium oxide (6.97 g.cm<sup>-3</sup>) and  $d_{RuO_2}$  is the mean diameter of the ruthenium oxide particle (nm).

Assuming the particle size in a spherical shape and using the formula described below (Eq. 3), the dispersion values were calculated as:

$$D_{Ru} = \frac{6 \times MA_{Ru} \times \sigma_{site_{Ru}}}{d_{Ru} \times \rho_{Ru} \times N_{av}}$$
(3)

where D is the dispersion (Ru surface/Ru total),  $\sigma_{Ru}$  is the density of the ruthenium active site  $(1.58\times10^{15}~atoms~cm^{-2})$ , considering as a single crystal, spherical shaped particles and formed from equal proportions of the main low index planes [45–47]; and  $N_{av}$  is the Avogadro constant  $(6.022\times10^{23}atoms.~mol^{-1})$ .

Specific surface area/porosity measurements of the supports and the different catalysts were conducted using a Quantachrome Instruments model Nova 2200e at 77 K at  $P/P_0 = 0.005$  to 0.99. The samples were pre-treated under vacuum at 373 K and remained at that temperature for 120 min, followed by 573 K for also 120 min and 623 K for 120 min.

The chemical composition of the catalysts was determined by using X-ray Fluorescence by Dispersive Energy (EDXRF) model S2 Ranger (Bruker) in helium flow, exposure time of 200 s, K $\alpha$  lines in 50 kV for ruthenium (filter Cu) and 40 kV for niobium (Al filter).

The programmed temperature reduction analysis (TPR-H<sub>2</sub>) was performed using a multi-purpose analytical system equipment coupled to a thermal conductivity detector (TCD). The samples were pretreated under a flow of argon (30 mL min<sup>-1</sup>) at 673 K for 30 min at a rate of 10 K min<sup>-1</sup>, cooled down and then submitted from 373 to 1073 K at a rate of 10 K min<sup>-1</sup> in a flow of H<sub>2</sub>/Ar (1.59 % mol), obtaining thus the thermograms for each material. The amount of theoretical H<sub>2</sub> needed to a complete reduction of Ru was estimated based on the Eq. 1 below:

$$\operatorname{RuO}_{2(c)} + \operatorname{H}_{2(c)} \to \operatorname{Ru}^{0}_{(s)} + \operatorname{H}_{2}\operatorname{O}_{(g)}$$

$$\tag{1}$$

The morphology of the samples was analyzed using a scanning electron microscope (SEM) JEOL JSM 6610 L V. The samples were deposited on a carbon tape and then metalized with a thin layer of gold in a vacuum using Denton Vacuum equipment model Desk V 15 kV.

X-ray photoelectron spectroscopy (XPS) spectra of the samples were performed using a PHI VersaProbe II Scanning XPS Microprobe with monochromatic X-ray Al Ka radiation as the excitation source (100 µm area analyzed, 52.8 W, 15 kV, 1486.6 eV) and the spectra were analyzed using PHI SmartSoft software and processed using MultiPak 9.3 package. The experiments were used to determine the chemical composition of the surface and the chemical state of the elements presented by the samples [48]. High-resolution spectra of C 1s, O 1s, Nb 3d, Ru 3d and Ru 3p for supports, fresh and used catalysts were recorded at a given take-off angle of 45° by a multi-channel hemispherical electron analyzer operating in the constant pass energy mode at 29.35 eV and the Au  $4f_{7/2}$ line was recorded with 0.73 eV FWHM at a binding energy (BE) of 84.0 eV, using a pressure in the analysis chamber lower than  $2.0 \times 10^{-6}$ Pa. Binding energies were corrected for charging by reference to the C 1s at 284.8 eV and the energy scale was calibrated using Cu  $2p_{3/2}$ , Ag  $3d_{5/2}$ , and Au  $4f_{7/2}$  photoelectron lines at 932.7, 368.2, and 83.95 eV, respectively. The recorded spectra were fitted using Gauss-Lorentz curves.

## 2.3. Catalytic tests

Prior to the reaction of glucose hydrogenation, the catalysts went on

to reduce their active phase. Each catalyst was placed in a glass reactor heated to 523 K with a heating rate of 10 K min<sup>-1</sup> under a continuous flow of 50 cm<sup>3</sup> min<sup>-1</sup> of 5 % H<sub>2</sub>/N<sub>2</sub> (White Martins, both 99.999 %) for 3 h. All the catalysts were characterized after the reduction of their active phases (5RuNb<sub>2</sub>O<sub>5</sub>\_A and 5RuNb<sub>2</sub>O<sub>5</sub>\_C).

After the reducing process, the catalyst sample was transferred to a Parr® model 4593 reactor (100 mL), with mechanical stirring and temperature and pressure controller, loaded with 50 mL of a 10 % glucose (D-glucose purchased from Sigma Aldrich  $\geq$  99.5 %) solution in ultrapure water (Mili-Q Integral water) and 500 mg of the catalyst. Subsequently, the system was purged with N<sub>2</sub> for 30 min to remove air and then pressurized with H<sub>2</sub> to 60 bar and heated to a temperature of 373 K. Once the set point was reached, the agitation was switched at 700 rpm, remaining for 4 h.

At the end of the reaction, the reaction product was properly filtered and analyzed through a quantitative determination of sugar (D-glucose purchased from Sigma Aldrich,  $\geq$  99.5 %), polyalcohol (D-sorbitol from Sigma Aldrich,  $\geq$  98 %) and 5-hydroxymethylfurfural (5-HMF from Sigma Aldrich,  $\geq$  99 %) by external standardization in a Hitachi Chromaster High-performance Liquid Chromatography (HPLC) coupled to a refractive index detector (IR) and an HPX-87H column (300 mm × 7.8 mm, Biorad), mobile phase 5 mM H2SO4 (0.5 mL min-1) and column temperature of 308 K. Glucose conversion, selectivity and yield to sorbitol were calculated according to Eqs. 4–6 below:

$$X (\%) = \frac{\text{mols glucose}_{\text{reacted}}}{\text{mols glucose}_{\text{initial}}} x 100$$
(4)

$$S (\%) = \frac{\text{mols}_{\text{sorbiol}}}{\text{mols glucose}_{\text{reacted}}} \times 100$$
(5)

$$Y(\%) = \frac{X * S}{100}$$
(6)

For the catalyst recycling experiments, after the end of each reaction, the solid catalysts were washed using ultrapure water and dried at 373 K for 12 h, being subsequently reduced in a flow of 5 %  $H_2/N_2$  and used in the reaction process.

# 3. Results and discussion

# 3.1. Characterization of catalysts

Fig. 1 shows the profile of the TG and DTA curves of Nb<sub>2</sub>O<sub>5</sub>.

Two clear thermal events are observed: the first event is indicated by an endothermic peak, at a temperature of 393 K, which is attributed to the mass loss due to the removal of physisorbed water on the oxide surface. The second event is characterized by the presence of an exothermic and sharp peak at 845 K, without significant mass loss and



Fig. 1. TG-DTA curves of Nb<sub>2</sub>O<sub>5</sub>.xH<sub>2</sub>O.

justified by the occurrence of a change from the amorphous phase to the crystalline phase of niobium oxide, known as the TT phase (pseudohexagonal phase), which presents a more orderly structure and intermediate to the formation of the T phase (orthorhombic phase) [49–52]. Between 573 and 873 K occurs the water elimination due to the condensation of the hydroxyl groups presented inside of the solid (bulk). From 873 K onwards, there is a tendency to stabilize mass loss by organizing the structure in the crystalline phase of niobium oxide [53]. The same behavior was also observed by Marin et al. [54] in the synthesis of amorphous nanostructured mesoporous Nb<sub>2</sub>O<sub>5</sub>. It showed that the thermal degradation of the materials is due to changes in physical properties, such as loss of the mesoporous structure and decrease of Brønsted acidity with the loss of coordination water molecules, generating new characteristics to the material.

The XRD patterns of the supports and catalysts are shown in Fig. 2. In the sample Nb<sub>2</sub>O<sub>5</sub>\_C (Fig. 2a), the presence of diffractions lines at  $2\theta = 22.1^{\circ}$  (001),  $28.1^{\circ}$  (100),  $36.6^{\circ}$  (101),  $46.2^{\circ}$  (002),  $50.6^{\circ}$  (110),  $55.2^{\circ}$  (102),  $56.1^{\circ}$  (111) and  $58.8^{\circ}$  (200) (JCPDS-28-0317) are characteristics of a pseudo hexagonal structure (TT phase) [49,55–57]. An increase in the heat treatment temperature of niobium oxide promotes an increase in the crystallinity of the material, given that the pseudo hexagonal phase is a modification of the T (orthorhombic) phase and a transitional phase between the amorphous phase and T phase [55].

For the amorphous sample (Nb<sub>2</sub>O<sub>5</sub>\_A) (Fig. 2c), no diffraction peaks are detected, but two broad and wide peaks around  $2\theta = 25$  and  $52^{\circ}$ , characteristic of the amorphous phase of niobium oxide, are observed [54].

For the calcined catalyst samples presented in Fig. 2a, the presence of a low-intensity peak around  $34.9^{\circ}$  can be indexed to the ruthenium

oxide (RuO<sub>2</sub>) in the (001) plane (JCPDS 88-0323). The same sample after the reduction process also shows a low-intensity peak close to 44°, which is indexed to Ru° in the hexagonal plane (101) (JCPDS 06-0663) [58]. It is also noticed that the peak referring to RuO<sub>2</sub> presents itself in a broad pattern. This pattern is associated with the formation of nanoparticles in the process of impregnation of the metal on the surface of niobium oxide. From the Scherrer equation (Eq. 1), it was possible to estimate that the particle diameter of this oxide was 9.2 nm. According to Eq. 2, the particle size for the metallic Ru was 7 nm and the dispersion of the Ru° particle (Eq. 3) of 18.7 %, which depicts the profile closest to the material during the reaction.

In the diffractograms of the calcined and reduced sample  $5Ru/Nb_2O_5_A$  (Fig. 2c), it is possible to identify small peaks referring to ruthenium oxide at 28.6, 35.8 and 54.8° and metallic ruthenium at 44.1° respectively. It can also be noted a more intense and sharper peak corresponding to the RuO<sub>2</sub> on this sample ( $5Ru/Nb_2O_5_A$  calcined) than on the crystalline and calcined sample  $5Ru/Nb_2O_5_C$ . This highest intensity and sharpest peak width in the synthesized catalysts may indicate the presence of larger particle size. However, on the  $5Ru/Nb_2O_5_C$ , the low intensity and the largest peak width in the synthesized catalysts are due to a high dispersion and a small particle size of the active metal over the niobium oxide [19,59].

Table 2 shows the compositions and textural properties of the prepared samples.

The results of the experimental composition obtained by EDFRX demonstrate that the wet impregnation technique is suitable for the preparation of catalysts with levels of 5% (w/w) of ruthenium.

An increase in the calcination temperature on the pure catalyst support provokes a reduction of the specific surface area from 95 to 15



Fig. 2. XRD patterns of Nb<sub>2</sub>O<sub>5</sub>\_C, 5RuNb<sub>2</sub>O<sub>5</sub>\_C calcined and reduced (a) e (b), and Nb<sub>2</sub>O<sub>5</sub>\_A and 5RuNb<sub>2</sub>O<sub>5</sub>\_A (c).

#### Table 2

Textural properties of catalysts and supports and chemical composition of the catalysts.

Catalysts	$\frac{S_{BET}}{(m^2 g^{-1})}$	$V_{P}^{b}$ (cm <sup>3</sup> g <sup>-1</sup> )	Pore Diameter (nm) <sup>c</sup>	Chemical Composition (%) <sup>d</sup> Ru
Nb <sub>2</sub> O <sub>5</sub> _A	95	0.149	3.7	-
5RuNb <sub>2</sub> O <sub>5</sub> _A	29	0.065	3.5	5.2
Nb <sub>2</sub> O <sub>5</sub> C	15	0.077	15.2	-
5RuNb <sub>2</sub> O <sub>5</sub> _C	17	0.096	15.2	4.8

 $^{\rm a}$  Calculated by BET method  $^{\rm b,c} {\rm Calculated}$  by BJH method (desorption branch).

Determined by EDXRF.

 $m^2 g^{-1}$  and in the pore volume from 0.149 to 0.077 cm<sup>3</sup> g<sup>-1</sup> and increase in the pore diameter from 3.5–15.2 nm. These results are in line with what was reported in the literature by Wang et al. [55]. The ruthenium impregnation process on the supports Nb<sub>2</sub>O<sub>5</sub>\_A and Nb<sub>2</sub>O<sub>5</sub>\_C only promoted a decrease in the specific surface area and pore volume on the niobium oxide in the amorphous phase.

The results for the  $N_2$  adsorption isotherm reflect the influence due to the heat treatment in the samples and indicate the effect of ruthenium impregnation on the textural properties of the material (Fig. 3).

The isotherms obtained for the support and the amorphous catalyst (Fig. 3a) are of type IVa, according to the classification presented by IUPAC. For the support and the crystalline catalyst (Fig. 3b) type II isotherms were obtained, characteristic of non-porous materials. The hysteresis loops verified in all samples resemble as type H3, characteristic of particle aggregates, and are formed between the relative pressures of 0.4 to 0.8 in amorphous samples (Fig. 3a) and between 0.5 and 0.99 for crystalline samples (Fig. 3b) [60–62].

The thermal treatment provokes a collapse of the structure and consequently rearrangements of the sites presented in the oxide. In the amorphous phase, the niobium oxide is formed by slightly and highly distorted NbO<sub>6</sub>, NbO<sub>7</sub> and NbO<sub>8</sub> sites. When the temperature increases, the structure is dehydrated by removing the coordination water molecules, leading to an increase in the distortion of the highly distorted NbO<sub>6</sub> octahedral sites [63–65].

The effect of ruthenium impregnation on the supports  $Nb_2O_5$  A and  $Nb_2O_5$  C on the textural properties are related to the presence of ruthenium particles that led to a decrease in the specific surface area and pore volume on the niobium oxide in the amorphous phase due to deposition of ruthenium particles clogging the micropores.

The increase in the found diameter allows a greater diffusion of glucose molecules, increasing the available surface area and more effective contact with the active phase.

The structural modifications are also detected by the morphological analysis obtained by SEM of the samples of the niobium oxide in the amorphous phase (Fig. 4a) and the crystalline phase (Fig. 4b), using 200x magnification.

The morphologies have an undefined format with the presence of large particle clusters and non-uniform distribution across the visualized area. In the sample of Nb<sub>2</sub>O<sub>5</sub>\_A (Fig. 4a), there are little dispersed particles with non-uniform distribution, indicated by the arrow. On the other hand, for Nb<sub>2</sub>O<sub>5</sub>\_C sample (Fig. 4b), a more defined and agglomerated aspect is observed. The small and dispersed particles resemble small rounded flakes in an irregular distribution, indicated by the arrow, favoring the formation of similar clusters in higher temperatures [56, 57]. Despite the non-uniform distribution of the particles for the two supports and the appearance of a mixed structure [66], the heat treatment at 873 K caused a greater proximity between the particles, impacting on the reduction of the specific surface area available for support [49].

For the samples of  $5Ru/Nb_2O_5_A$  and  $5Ru/Nb_2O_5_C$  (Figs. 5a and 5b, respectively), no morphology changes are noticed after the process of impregnation and calcination of the material due to the small size of Ru particles dispersed in the material.

The results demonstrate that the phase change of Nb<sub>2</sub>O<sub>5</sub> leads to an arrangement of the unit cells of the material. The same behavior was perceived by Chan et al. [63] when evaluating the use of niobium oxide at different temperatures in the dehydration reaction of furfuryl alcohol, obtaining surface areas between 130 m<sup>2</sup> g<sup>-1</sup> and 5 m<sup>2</sup> g<sup>-1</sup>, and Wang et al. [55] in the preparation Nb<sub>2</sub>O<sub>5</sub> with different calcination temperatures, obtaining values of 142 m<sup>2</sup> g<sup>-1</sup> (673 K) and 17.6 m<sup>2</sup> g<sup>-1</sup> (873 K).

In the TPR-H<sub>2</sub> thermograms, shown in Fig. 6, the reducibility of Ru supported on niobium oxide was evaluated and the results were summarized in Table 3.

The catalyst reduction profiles are related to parameters of the type of metal used and the adsorption force of the active sites to hydrogen, indicating stronger interactions between the metal and support [59,67]. The sample 5RuNb<sub>2</sub>O<sub>5</sub>\_A has a profile on a broader format with the presence of two characteristic peaks around 454 and 481 K, and three small shoulders peaks at 405, 515 and 823 K. The small shoulder peak observed at 405 K can be attributed to the probable reduction of the residual RuCl<sub>3</sub> salt used as a precursor for the synthesis [24,68,69]. The small shoulders peaks formed in 515 and 823 K were attributed to the reduction of smaller Ru particles in the catalyst with stronger interaction between the support and smaller particle sizes [70].

The first characteristic peak at 454 K can be attributed to intermediate species of ruthenium oxide ( $Ru_2O_3$  and RuO) formed during the  $RuO_2$  reduction steps or the presence of particles of different sizes of



Fig. 3. Nitrogen adsorption isotherms at 77 K and pore size distribution of the supports and catalysts.



Fig. 4. Scanning micrographs of Nb<sub>2</sub>O<sub>5</sub>A (a) and Nb<sub>2</sub>O<sub>5</sub>C (b) with 200x magnification.



Fig. 5. Scanning micrographs of the 5Ru/Nb<sub>2</sub>O<sub>5</sub>A (a) and 5Ru/Nb<sub>2</sub>O<sub>5</sub>C (b) with 10000x magnification.



Fig. 6. TPR-H<sub>2</sub> profile for the catalysts.

RuO<sub>2</sub> [71,72].

For the catalyst 5RuNb<sub>2</sub>O<sub>5</sub>\_C, shoulders peaks were detected at 408 and 442 K, and a sharp peak at 460 K. Possibly, these shoulders are related to the reduction of different intermediate species of RuO<sub>x</sub> (Ru<sup>3+</sup> and Ru<sup>2+</sup>) as observed in the catalyst 5RuNb<sub>2</sub>O<sub>5</sub>\_A. The peak at 460 K can be attributed to the reduction of Ru<sup>4+</sup> to Ru° [59].

The hydrogen consumption values were very close to samples

Table 3
---------

H<sub>2</sub> consumption calculated from TPR-H<sub>2</sub> measurements of Ru catalysts.

Catalyst	Maximum Temperature (K)	Stoichiometric $H_2$ consumption <sup>a</sup> (µmols g <sub>cat</sub> <sup>-1</sup> )	$H_2$ consumption (µmols $g_{cat}^{-1}$ )
5RuNb <sub>2</sub> O <sub>5</sub> _A	454 / 481	276.2	423.6
5RuNb <sub>2</sub> O <sub>5</sub> _C	460	276.9	477.8
3 **			

<sup>a</sup> H<sub>2</sub> consumption calculated theoretically.

# 5RuNb<sub>2</sub>O<sub>5</sub>\_A and 5RuNb<sub>2</sub>O<sub>5</sub>\_C, as shown in Table 3.

The obtained results indicate that during the reduction process, a metallic ion is formed in a reduced state ( $Ru^\circ$ ) for its use in the hydrogenation reaction. It is noted that there was an experimental hydrogen consumption higher than stoichiometric consumption [58]. This consumption can be attributed to the migration of H atoms to the support (spillover effect), which can favor the reaction process due to the greater availability of active centers by the material [28]. The Nb<sub>2</sub>O<sub>5</sub> support requires temperatures above 1073 K for its reduction [33,73], which is confirmed by the rise of the baseline over 900 K in the H<sub>2</sub>-TPR profiles obtained from the amorphous and crystalline samples [59,67,73].

# 3.2. Catalytic tests

Fig. 7 provides the conversion and selectivity data to sorbitol during the hydrogenation reaction of glucose at 373 K and 60 bar during 4 h of reaction using the synthesized catalysts and supports.

The use of the amorphous phase support (Nb<sub>2</sub>O<sub>5</sub>A) provided a small



**Fig. 7.** Conversion of Glucose and Selectivity to Sorbitol using ruthenium catalysts supported on niobium oxide in amorphous phase (a) and crystalline phase (TT phase) (b). Reaction condition: glucose (10 % w/w), 500 mg of catalyst, 373 K and 60 bar of  $H_2$ .

increase in carbohydrate conversion in comparison to the reaction without using a catalyst. This increase is attributed to the higher reactivity of the material, due to the textural properties such as high surface area, and the relationship between the acid sites of Brønsted and Lewis on the surface [55]. It can also be noted a low conversion of glucose during the reaction using the support without the formation of sorbitol. However, it was perceived a color change from white to light brown of the solid catalyst after the reaction, indicating the formation of humines and their deposition on the surface of the material.

As a result of the reactions with catalysts reduced under  $5 \% H_2/95 \%$  N<sub>2</sub> flow for 3 h, differences between conversions and selectivities were detected in the use of amorphous and crystalline structures for niobium oxide. When using the amorphous catalyst, the substrate conversion achieved was 31.3 %, while the selectivity to the desired product was 77.2 %. For the recycle tests, it can be noticed a high decrease in conversion and selectivity, 8 % and 7 % respectively, after three cycles. In the use of support in crystalline form, the catalyst  $5RuNb_2O_5\_C$  showed an increase in glucose conversion to 84.6 % and selectivity of 98 % to sorbitol. The increase in conversion is represented by the increase in the activity of the catalyst when using a more ordered structure and transitional of the oxide (TT phase) [63]. Contrary to the amorphous catalyst, it was noted that the crystalline catalyst maintains a high selectivity to sorbitol and conversion of glucose, 98 % and 82 % after the second and third cycle, respectively.

Mejía et al. [41] reported that  $Nb_2O_5$  supported Co catalyst in its crystalline form increased the catalytic activity in Fischer-Tropsch reactions when compared to its amorphous state, although there had been

a decrease in the volume of pores, surface area, and transformation into a denser structure. The authors concluded that, in the preparation of an active catalyst for this reaction, the crystallization of niobia needs to be performed at temperatures over 400 °C, before Co deposition, and that this procedure allows the formation of reducible cobalt oxide species. The herein observed profile was analyzed by the BET and BJH methods (Table 2), which showed that the crystalline Ru/Nb<sub>2</sub>O<sub>5</sub> catalyst presents pores of smaller volumes, however, with larger diameters.

The low conversion of glucose presented by the sample  $5RuNb_2O_5_A$  can be explained by the presence of an amorphous and irregular structure of the support, which does not allow the accessibility of the glucose molecules to the ruthenium particles within the mesopores in the catalyst [41]. As evidenced by the N<sub>2</sub> isotherm analysis, the catalyst in the crystalline phase has a smaller surface area, but a larger pore diameter (15 nm), alongside the presence of a more defined and ordered structure of the catalyst, as noticed in the analysis of SEM. This structural modification allowed better accessibility by the glucose molecules (d = 0.65 mm) to the ruthenium particles, favoring the adsorption at the sites, which may explain the high glucose conversion. Besides, the influence of the support structure on glucose conversion and selectivity to sorbitol is due to the difficulty in activating it as shown by the TPR-H<sub>2</sub> analysis, in which there is a small distance from the peak related to the reduction of ruthenium oxide at a higher temperature.

The XPS study of the supports and the catalysts before and after catalysis can give relevant information. Fig. 8 shows the Nb 3*d* core level spectra of the supports and the catalysts, and Table 4 includes the binding energy values of the Nb  $3d_{5/2}$  peaks with their correspondent FWHM values. It is clear that all spectra are very similar, with binding energy values in a range of 207.2–207.6 eV, typical of Nb<sup>5+</sup> [74]. However, as expected, the FWHM values when crystalline Nb<sub>2</sub>O<sub>5</sub> is used are lower, even when Ru is incorporated and after catalysis. These data confirm the stability of the support.

The chemical composition of the surface of supports and catalysts before and after catalysis is included in Table 5. In this Table, some interesting facts are observed. Firstly, the O/Nb atomic ratio for the supports Nb<sub>2</sub>O<sub>5</sub>\_A and Nb<sub>2</sub>O<sub>5</sub>\_C are 2.51 and 2.45, respectively. These values are very near to the theoretical O/Nb value (2.50), indicating that the composition at the surface is near to the bulk. Secondly, chlorine is not detected at the surface. However, the most interesting fact is the evolution of the atomic concentration of Ru. In both cases, the content of Ru in the catalysts increased after catalysis from 2.95 % to 3.59 % in the case of sample 5RuNb<sub>2</sub>O<sub>5</sub>\_A, and from 1.94 % to 7.36 % in the case of sample 5RuNb<sub>2</sub>O<sub>5</sub>\_A, from 0.147 to 0.182 for sample 5RuNb<sub>2</sub>O<sub>5</sub>\_A, A



Fig. 8. Nb 3d core level spectra of samples (A) Nb<sub>2</sub>O<sub>5</sub>\_A, (B) Nb<sub>2</sub>O<sub>5</sub>\_C, (C) 5RuNb<sub>2</sub>O<sub>5</sub>\_A, (D) 5RuNb<sub>2</sub>O<sub>5</sub>\_C, (E) 5RuNb<sub>2</sub>O<sub>5</sub>\_A used and (F) 5RuNb<sub>2</sub>O<sub>5</sub>\_C used.

## Table 4

Binding energy values (in eV) of the signals Nb  $3d_{5/2}$  and Ru  $3p_{3/2}$ .

	-		
Sample	Nb 3 <i>d</i> <sub>5/2</sub>	FWHM	Ru 3p <sub>3/2</sub>
Nb <sub>2</sub> O <sub>5</sub> _A	207.2 eV	1.11 eV	-
Nb <sub>2</sub> O <sub>5</sub> C	207.2 eV	1.04 eV	-
5RuNb <sub>2</sub> O <sub>5</sub> _A	207.6 eV	1.27 eV	461.8 eV
5RuNb <sub>2</sub> O <sub>5</sub> C	207.2 eV	1.08 eV	461.7 eV
EBuNh O A used	207.5 eV	1.02 .1	461.3 eV (66 %)
5RuND <sub>2</sub> O <sub>5</sub> _A used		1.25 eV	462.8 eV (34 %)
EBuNh O. Cured	207 E oV	1 15 oV	461.6 eV (82 %)
$5$ KuND <sub>2</sub> O <sub>5</sub> _C used	207.3 ev	1.15 eV	463.7 eV (18 %)

# Table 5

Chemical composition (in atomic concentration %) of studied supports and catalysts.

Sample	C 1s	O 1s	Nb 3d	Ru 3p <sub>3/2</sub>	Ru/Nb
Nb <sub>2</sub> O <sub>5</sub> _A	21.06	56.43	22.55		
5RuNb <sub>2</sub> O <sub>5</sub> _A	20.12	56.89	20.05	2.95	0.147
5RuNb <sub>2</sub> O <sub>5</sub> C	11.82	64.04	24.20	1.94	0,080
5RuNb <sub>2</sub> O <sub>5</sub> _C used	26.28	49.44	16.93	7.36	0.435

and from 0.080 to 0.435 for sample  $5RuNb_2O_5$ \_C. This large change in the Ru/Nb ratio can be attributed to the segregation of Ru to the surface of the catalyst due to the difference in surface area of the support Nb<sub>2</sub>O<sub>5</sub>\_C, which is much lower than Nb<sub>2</sub>O<sub>5</sub>\_A.

The chemical state of ruthenium on the surface can be studied by XPS by considering Ru 3*d* and Ru 3*p*<sub>3/2</sub> core level spectra. However, the Ru 3*d* spectra are partially overlapped with the C 1*s* signal, and it is better to use the Ru 3*p*<sub>3/2</sub> signal. Fig. 9 shows the Ru 3*p*<sub>3/2</sub> core level spectra for catalysts 5RuNb<sub>2</sub>O<sub>5</sub>\_A and 5RuNb<sub>2</sub>O<sub>5</sub>\_C, before and after catalysis, and Table 4 indicates the binding energy values of the different chemical states of Ru. In the case of catalysts 5RuNb<sub>2</sub>O<sub>5</sub>\_A, before catalysis, the Ru 3*p*<sub>3/2</sub> signal can be fitted with a single contribution at 461.8 eV, assigned to Ru<sup>0</sup> [75]. The used catalysts present a broader Ru 3*p*<sub>3/2</sub> signal that can be deconvoluted in two contributions at 461.3 eV (66 %) and 462.8 eV (34 %). The former assigned to Ru<sup>0</sup> and the later to Ru<sup>3+</sup> [76].

In the case of catalyst  $5RuNb_2O_5_C$ , similar facts were observed with a single contribution at 461.7 eV before catalysis, and with two contributions after catalysis, but in this case, the contribution at high binding energy appears at 463.7 eV and with a lower relative intensity (18 %). This high binding energy is typical of  $Ru^{4+}$  [75]. The data aforementioned indicate that catalyst  $5RuNb_2O_5_C$  presents a much higher content of Ru after catalysis and almost all ruthenium is as  $Ru^0$ , explaining its much better observed catalytic performance in the conversion of glucose to sorbitol.

## 4. Conclusions

The preparation of catalysts containing Nb<sub>2</sub>O<sub>5</sub> calcined at different temperatures followed by wet impregnation with RuCl<sub>3</sub> led to a catalyst with high yield in the hydrogenation of glucose into sorbitol. For the thermal treatments used in the study of niobium oxide as catalytic support for hydrogenation reactions, a decrease in surface areas and pore volume was observed, also the effectiveness in reducing the residual chlorine content present by using heat treatment after impregnation. In the reaction conditions, the results obtained indicate that the structural alteration of the catalysts had a distinctly positive effect on the selectivity of ruthenium and the conversion of glucose into the liquid phase. The use of the crystalline phase (TT phase) for the catalytic support showed a conversion around 85 % and selectivity of 98 %, while the same material in the amorphous phase showed a conversion less than and equal to 52.5 % and selectivity of 54.9 %. This observed behavior can be explained by the potential presented by the



**Fig. 9.** Ru  $3p_{3/2}$  core level spectra of samples  $5RuNb_2O_5A$ ,  $5RuNb_2O_5A$  used,  $5RuNb_2O_5C$  and  $5RuNb_2O_5C$  used.

modification of the structure obtained after heat treatment, which facilitated the reaction between the substrate and active sites present internally in the pores of the material. The study by XPS of the catalysts before and after catalysis explains the better catalytic performance of sample  $5RuNb_2O_{5-}C$  in the conversion of glucose to sorbitol.

### **CRediT** authorship contribution statement

Jordan Gonzaga Andrade Batista Silva: Conceptualization, Methodology, Formal analysis, Writing - original draft. Ronaldo Costa Santos: Validation, Formal analysis, Data curation, Writing - review & editing. Enrique Rodríguez-Castellón: Methodology, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. Leonardo Sena Gomes Teixeira: Conceptualization, Validation, Data curation, Writing - review & editing, Supervision. Luiz Antônio Magalhães Pontes: Conceptualization, Data curation, Writing - review & editing, Supervision, Project administration.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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