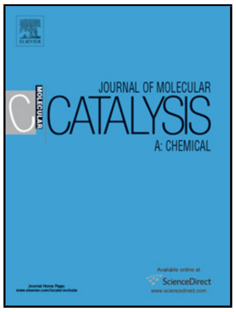

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Enhanced catalytic activity for fructose conversion on nanostructured niobium oxide after hydrothermal treatment: Effect of morphology and porous structure

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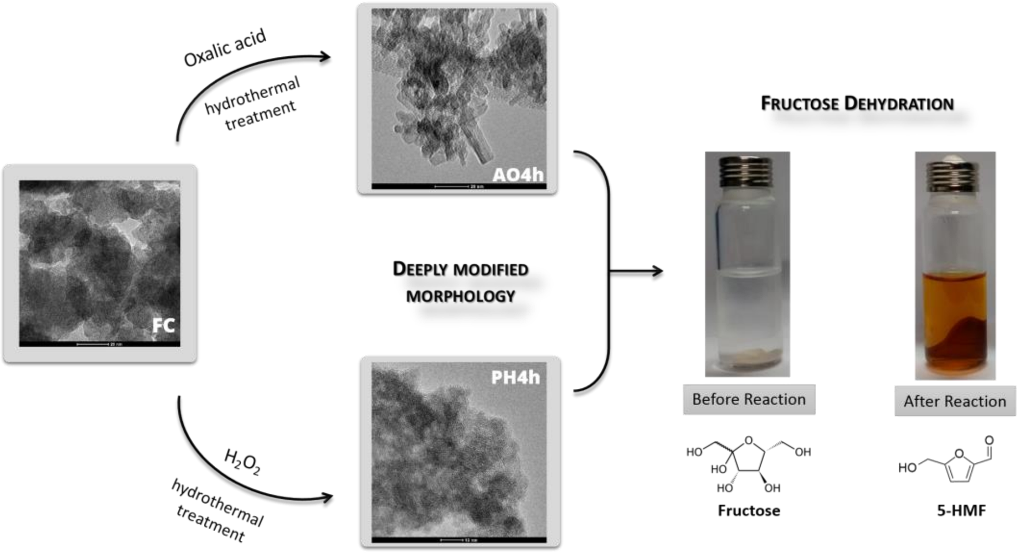
Graphical Abstract



Synopsis: A new class of catalysts based on niobium was hydrothermally synthesized using Filter Cake (FC) as a precursor. The use of different agents (oxalic acid or hydrogen peroxide) allowed the obtention of nanostructured materials in the form of rods or spheres with larger BET area, crystallinity and acidity than the precursor. Their potential was evaluated in fructose dehydration reaction in aqueous media and in DMSO, obtaining 22% and 47% yield of 5-HMF, respectively.

Highlights

- A new class of catalysts based on niobium was hydrothermally synthesized using Filter Cake as a precursor.
- The use of different agents (oxalic acid or hydrogen peroxide) allowed the formation of nanostructured materials in the form of rods or spheres.
- Their potential was evaluated in fructose dehydration reaction obtaining 41% yield of 5-HMF.

Abstract

This paper reports the synthesis of a new class of catalysts based on niobium using Filter Cake (FC) as precursor, which is more affordable economically than other niobium sources commonly used. FC is obtained before the necessary purification to obtain niobic acid ($Nb_2O_5.nH_2O$), making the catalyst synthesis process less costly. Its modification by hydrothermal treatment in the presence of different agents (oxalic acid or hydrogen peroxide) allowed the obtention of nanostructured materials in the form of rods or spheres with larger BET area, crystallinity and acidity than the precursor. Their catalytic potential were evaluated in fructose dehydration reaction in aqueous media, aiming the obtention of 5-hydroxymethylfurfural (5-HMF). The production of furan compounds from sugars has become a process of great interest in recent years because it is related to the search for more sustainable sources of energy, since carbohydrates are the predominant part of biomass. In optimum conditions, it was possible to obtain 22% yield of 5-HMF in aqueous medium and 47% yield of 5-HMF using DMSO as solvent.

Keywords: Niobium oxide; fructose; dehydration; 5-hydroxymethylfurfural

1. INTRODUCTION

The use of biomass for obtaining chemical derivatives and fuels has emerged as an important research area in recent years due to the fact that it is a renewable source of great abundance.[1], [2]

In particular, the carbohydrate class - predominant compounds in the biomass - shows considerable potential to provide important intermediates for the chemical industry. However, the economic feasibility of processes based on the use of biomass critically depends on the selectivity of the products obtained, since the carbohydrates are highly functionalized molecules and therefore, can undergo a variety of reactions.[3]

Carbohydrates dehydration leads to the formation of furan compounds such as furfural and 5-hydroxymethylfurfural (5-HMF), which are key intermediates for obtaining several products of petrochemical interest.[4]

5-HMF is a compound consisting of a furan ring containing an aldehyde group and a hydroxymethyl group at positions 2 and 5. It can be obtained through three dehydration reactions of carbohydrates C-6 and C-5 derived from biomass and might act as a green chemical intermediate for obtention of a wide range of compounds current from petroleum.[4]

Rehydration of 5-HMF enables the obtention of levulinic acid and formic acid, which are commodity chemicals. Furthermore, the levulinic acid is the precursor of liquid fuel γ-valerolactone. The oxidation of the hydroxymethyl group allows the obtention of 2,5-diformylfuran and 2,5-furandicarboxylic acid (FDCA). FDCA is particularly interesting as a polymeric replacement for terephthalic and isophthalic acids which are used to obtain polyamides, polyesters and polyurethanes.[5]

5-HMF may also suffer undesirable degradation and polymerization to form insoluble polymers known as humins through reaction with itself and with other monosaccharides.[6]

Therefore, an efficient production of 5-HMF requires minimization of undesirable side reactions, such as its rehydration. This influences the efficiency of the process and the generation of humins, which has been identified as the main cause of the low 5-HMF yields reported in the majority of papers present in the literature.

In view of the above, different homogeneous and heterogeneous catalysts have been applied in this reaction. Solid acid catalysts have been widely studied due to their high acidity, easy separation from the reaction medium, reusability, among other properties. In particular, the use of systems based on niobium oxide (Nb_2O_5) have played an important role in various catalytic reactions due to its high acidity and catalytic stability.

Wang et al. evaluated the catalytic activity of mesoporous niobium phosphate on fructose dehydration using water as solvent and obtained a maximum yield of 45% for 5-HMF and 58% of fructose conversion in optimal conditions (130°C, 30 minutes).[7] Nb_2O_5 obtained by the calcination of niobium acid in a temperature of 400°C allowed total fructose conversion with yield of 86% for 5-HMF using DMSO as solvent at 120°C for 2 hours.[8]

Such examples demonstrate the great potential possessed by niobium-based systems. However, its preparation in the form of nanocrystals with high surface area and acidity still represents a big challenge. Some synthesis methodologies that aim the obtention of niobium nanoparticles have been used, such as the sol-gel method followed by calcination or precipitation method in aqueous ammonia.[9–12] However, the crystallization promoted under hydrothermal conditions has been identified as a good strategy to obtain nanocrystals of metal oxide using milder temperatures and reaction conditions.

Therefore, we report in this work the synthesis of a new class of catalysts obtained from the hydrothermal treatment of the precursor Filter Cake (FC) with oxalic acid or hydrogen peroxide and their use in the dehydration reaction of fructose in aqueous medium.

2. EXPERIMENTAL

2.1 Synthesis of Catalysts

2.1.1. Thermal treatment in presence of oxalic acid

The synthesis of Nb_2O_5 nanoparticles was performed using the hydrothermal method using stainless steel autoclave BERGHOF® BR-100 containing Teflon cup and magnetic stirrer set at 300 rpm. 1g of the precursor material (Filter Cake, kindly supplied by CBMM) was dispersed in 40 mL of oxalic acid aqueous solution (0.2 mol/L). The suspension was placed in hydrothermal cell and the temperature adjusted to 220°C and autogenous pressure. The studied times of the hydrothermal treatment were 4 and 12h, and the materials identified as AO4h and AO12h, respectively. A white solid was obtained as a final product, which was washed with distilled water until pH=7, centrifuged and dried at 70°C for 12 hours.

2.1.2. Thermal treatment in presence of H_2O_2

For this synthesis, 1g of precursor material (Filter Cake) was dispersed in 40 mL of water. To this dispersion, hydrogen peroxide (Synth, 50% v/v) was added in a molar ratio of 10:1 H_2O_2:Nb, resulting in a yellow color, which is indicative of the niobium-peroxo complex formation. The hydrothermal treatment was carried out at 150°C at autogenous pressure and times of 4 and 12h were evaluated, being the materials identified as PH4h and PH12h, respectively. In the end, a white solid was obtained and washed with distilled water until pH=7, centrifuged and dried at 70°C for 12 hours.

2.2. Catalytic Reactions

The fructose dehydration reactions were conducted in batch mode using a 15mL glass reactor with a stainless steel screw top under autogenous pressure and constant magnetic agitation (500 rpm). In a typical run, 10mL of fructose aqueous solution (20, 40 or 60 g/L) was placed in contact with the appropriate amount of catalyst (0.1 or 0.2g). Time zero was noted when the temperature reached the adequate value (35, 70 or 130ºC). After the reaction time, the reactor was quickly submerged in a water bath cooled with ice. After cooling, the sample was centrifuged and the supernatant liquid was analyzed by gas chromatography-mass spectrometry and high-performance liquid chromatography, as described below. The reaction conditions used were chosen based on other studies[13], where they obtained significant results of conversion and selectivity. For reuse tests, the catalyst was rinsed with water, separated by centrifugation and dried at 100ºC for 3h. Then, the catalyst was again tested under the same experimental conditions used in the original reaction system.

2.3. Products Characterization

The remaining fructose concentration was determined using calibration curve through high-performance liquid chromatography with refractive index detector Waters 410 and Supelco Nucleosil 100 NH_2 5µm (25 cm × 4.6 mm) column. Acetonitrile: water (60:40) was used as mobile phase at a flow rate of 1.0 mL min^{-1}.

The products obtained were analyzed by gas chromatography-mass spectrometry using the equipment Agilent, HP-5MS column (5% polymethylphenylsiloxane) 30 m x 250 µm x 0.25 µm. The temperature profile used for the heating furnace was initially set to 40°C with permanence of 1 minute, and then increased to 90°C at a heating rate of 3°C/min, and maintained at that temperature for 10 minutes.

The concentration of 5-HMF was determined by calibration curve. The product yield and the fructose conversion were based on the initial sugar concentration and calculated as:

$$Yield = \frac{Product\ Concentration}{Fructose\ initial\ concentration}\ x\ 100$$

$$Fructose\ conversion = \left(1 - \frac{Fructose\ concentration}{Fructose\ initial\ concentration}\right)\ x\ 100$$

For reactions using DMSO as solvent, NMR spectroscopy was also used to characterize the products. 300µL of the reaction product and 200µL DMSO-d_6 containing gallic acid as internal standard (1.50 mg.mL^{-1}) were transferred to 5 mm NMR tube for analysis. ^{1}H NMR experiments were carried out on a Bruker Avance DRX400 (9.4Tesla) equipped with an inverse multinuclear 5 mm probehead. An exponential weighting function corresponding to 0.3 Hz line broadening was applied to the free induction decay before applying Fourier transformation. The spectra were processed and analyzed using TopSpin 1.3 software. ^{13}C NMR experiment as well as the following two-dimensional NMR spectra were also obtained (HSQC (heteronuclear single-quantum coherence – ^{1}H x ^{13}C) and HMBC (heteronuclear multiplebond correlation – ^{1}H x ^{13}C)).

2.4. Characterization of the materials

The X-ray diffraction patterns were obtained on a Shimadzu equipment, model XRD-7000 X-ray diffractometer, equipped with copper tube, 30 mA current and 30 kV voltage. The scan rate used was 4° min^{-1}.

The analyses of transmission electron microscopy (TEM) were performed at the Microscopy Center-UFMG using the Transmission Electron Microscope Tecnai G2-20-SuperTwin FEI-200 kV.

Thermogravimetric analyses were performed using the Shimadzu-TGA50H equipment. About 3.0 mg of the sample was continuously heated in a temperature range of 25 to 700°C with a heating rate of 10°C min^{-1} in air atmosphere and flow of 50 mL min^{-1}.

The Raman scattering measurements were performed at room temperature in a Bruker-Senterra apparatus using a 532 nm laser with 10 mW power, a laser aperture of 50 µm and 50x magnification objective, an integration time of 10s and 15 co-additions.

The textural properties of the materials were evaluated by the technique of adsorption/desorption of nitrogen at 77K using the Quantachrome Autosorb iQ$_2$ equipment. The specific surface area was calculated using the BET method in a low relative pressure region. The pore size distribution was calculated from the isotherm using the BJH model.

The acidity properties of the catalysts were characterized by Temperature Programmed Desorption method (TPD) using NH_3 as probe molecule. A Quantachrome ChemBET-3000 equipment containing TCD detector using a current of 150 mA and an attenuation of 32 was used. Approximately 0.2 g of catalyst was treated at 100°C for 60 min in a continuous flow of helium (80 mLmin^{-1}) and NH_3 adsorption was then held at 50°C. The TPD-NH_3 profiles were obtained at a heating rate of 10°C min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Characterization of the catalysts

Figure 1 shows the diffraction patterns of X-ray for samples subjected to hydrothermal treatment as well as the precursor Filter Cake. The patterns resemble the monoclinic system Nb_2O_5 reported by Tamura et al.[14] as well as the orthorhombic system of hydroxide niobium oxide ($Nb_3O_7(OH)$) according to Izumi et al.[15] The characteristic peak at $2\Theta = 22.54^o$ corresponds to the system hkl (0 4 0).

The increase in crystallinity observed after the treatment can be attributed to the rearrangement of the niobium's polyhedral units caused by the occurrence of dissolution and recrystallization during the process of hydrothermal synthesis.[16] Furthermore, according to the literature,[17] the presence of oxalic acid prevents the formation of skewed chains due to their chelation to metal polyhedra through oxygen atoms, that is, the two carboxyl groups of the oxalic acid would assist in preventing the disorderly polycondensation when binding to the metal center (Figure 2), helping to control nucleation and morphology.

The materials were analyzed by thermogravimetry upon heating in room atmosphere. The results are shown in Figure 3.

Analyses by thermogravimetry allowed to observe a common mass loss event for all catalysts in a temperature range up to 100°C, approximately. This result can be attributed to the loss of adsorbed water on the oxide surface.

The materials treated with hydrogen peroxide also showed a second mass loss event at a temperature of approximately 170^{o}C, as can be observed in the DTG curves. This event should be associated with the decomposition of the peroxo groups, as reported by Passoni et al.[18] This result demonstrates, therefore, that peroxo groups were incorporated into the material by the utilization of hydrogen peroxide. This is very interesting since several authors show that the peroxo group is highly active in several types of catalytic reactions.[19–21]

Moreover, no mass loss events were observed due to the decomposition of organic matter, demonstrating that all oxalic acid has been hydrolyzed during the process.

Thermogravimetric analysis also shows that the catalysts are thermally stable at the temperatures chosen for the reaction tests.

Raman spectroscopy was performed to confirm the niobium oxide structure of the catalysts. Its importance lies in the fact that this technique is very sensitive to the structure and binding order of metal oxides, especially in the region corresponding to the metal-oxygen stretching modes.[22] In this way, Figure 4 shows the Raman spectrum of the catalysts.

Most of the compounds based on niobium oxide have NbO_6 octahedral structures, which have distortions, so observed bands in the region 500-800 cm^{-1} correspond to stretching NbO_6 structures slightly distorted. The presence of bands is also observed in the region 200-300 cm^{-1}, which are assigned to angular deformation modes of Nb-O-Nb. The presence of bands in a higher frequency region is related to a higher niobium-oxygen bond order. Thus, the bands observed in the region of 900-1200 cm^{-1} are assigned to the symmetric stretching mode of Nb=O surface sites. The fact that the band observed at approximately 992cm^{-1} is well defined is related to the presence of a more ordered structure, which is in accordance with the certain degree of crystallinity presented by materials as evidenced by X-ray diffractometry analyses.[23–25]

Figure 5 shows the transmission electron microscopy images (TEM) of the niobium oxides synthesized under hydrothermal conditions and also the precursor Filter Cake. These images clearly show that the use of oxalic acid strongly influenced the structural features and the particle size. Nanorods with approximately 5nm of diameter were formed upon oxalic acid treatment.

The interplanar spacing of 0.394 nm for the catalyst AO4h corresponds to the (0 4 0) plane related to Nb_2O_5 phase, which relates to the maximum peak intensity in $2\Theta = 22.54°$ observed in the XRD analysis.[14]

A similar morphology has been described for tungsten and titanium oxides also synthesized under hydrothermal conditions in the presence of oxalic acid.[26],[27] However, the fact that the growth mechanism allowed the obtention of nanorods is not yet well understood.[17]

Figure 5 also shows that the PH4h and PH12h catalysts have spherical nanoparticles agglomerates containing crystalline regions, which is the same morphology observed by Leite et al.[28] using a similar synthesis procedure. The use of H_2O_2 in combination with the hydrothermal treatment has the advantage of obtaining crystalline nanomaterials under mild reaction conditions besides being a clean method due to absence of any potentially toxic by-product or contaminants that could interfere in the catalytic tests. The results obtained by transmission electron microscopy show that the precursor Filter Cake had their morphology deeply modified by the addition of H_2O_2 or oxalic acid. The modification performed under mild hydrothermal conditions can significantly affect their catalytic properties, since some reactions are sensitive to morphology and type of defects generated on the surface of catalysts.

It is also important to mention that the majority of the studies in the literature use more drastic reaction conditions and different precursors to obtain nanomaterials based on Nb_2O_5. For example, Lu et al.[29] obtained Nb_2O_5 nanorods by hydrothermal treatment of metallic Nb powder for three days in an autoclave. This way, obtainment of Nb_2O_5 nanoparticles of 5nm order using Filter Cake in the presence of oxalic acid and mild reaction conditions is not reported in the literature.

The textural properties of the catalysts are summarized in Table 1. N_2 adsorption/desorption isotherms (a) and the pore size distribution profile (b) obtained by the Barrett-Joyner-Halenda method (BJH) are shown in Figure 6. As observed in the morphology changes, hydrothermal treatment has also promoted a strong modification in the porous structure. As a result, the new catalysts showed higher BET area than the precursor Filter Cake (Table 1). All the isotherms were classified as type IV according to the IUPAC classification, which is assigned to the multilayer adsorption of mesoporous solids.[30] It is noteworthy that the PH12h catalyst exhibits a hysteresis that can be classified as type H2, very common for porous inorganic oxides, being attributed to the pore connectivity effects.[31] Treatment with H_2O_2 showed a more severe modification, generating pores with radio between 18 to 48 Å. These pore sizes can facilitate the diffusion of larger molecules to the active sites and consequently favor the catalytic process.

Besides that, it is known that the acidity of the materials is of fundamental importance for the sugars conversion study into 5-HMF. Due to this, the materials were also characterized by temperature programmed desorption of ammonia (TPD-NH_3) (Figure 7).

The TPD-NH_3 experiment was carried out to evaluate the change in total acidity and acid strength after the hydrothermal treatment. The temperature at which ammonia desorbs determines the strength of the acid sites. Based on this desorption temperature, the acid sites can be classified as weak (100- 200°C), moderate (200-400°C) and strong (> 400°C).[33] From the

TPD-NH_3 profiles (Figure 7) and Table 1 it is possible to observe that the hydrothermal treatment provided an increase in total acidity, so that the AO4h catalyst has the largest integrated area under the curve, indicating greater desorption of ammonia and higher acidity compared to the other catalysts and to the precursor Filter Cake.

Though the total acidity of Filter Cake is much lower than the other samples hydrothermally treated, the acid sites showed higher acid strength. The lower temperature shift upon treatment might indicate a surface modification of the acid sites which weakly bond with ammonia. The total acidity increase upon treatment might be related to the increase of BET area and also to the morphology change, which might play an important role in how this sites can be available.

Another aspect that can be observed is the decrease of the number of acid sites with the increase of hydrothermal treatment time. Such behavior may be related to the reduction of BET area, described above.

On the other hand, the catalysts treated with H_2O_2 present practically only strong sites and also a smaller number of acid sites. Furthermore, the reduction in area shown by peaks at about 300°C may be related to the generation of peroxo groups, which replaces acid groups in materials.[34] The moderate acidity indicated by the peak in the region of 200 to 400°C can be attributed to Brønsted acid sites.[35] This way, the reduction of that peak area is related to the reaction of the Brønsted acid sites with hydrogen peroxide to generate the oxidant groups.

Comparatively , the acidity of the catalysts reported here was higher than, or similar to, those obtained by other authors, who also using a hydrothermal synthesis, obtained niobium oxide from the precursor niobic acid ($Nb_2O_5.nH_2O$).[16] In that case, the treatment was conducted at a temperature of 135ºC for 3 days and the amount of Nb used corresponding to 0.25 mmol. The material was then calcined at 400°C for 4h in air atmosphere and presented a number of acid sites of 25 μmol g^{-1}. The author also reports the hydrothermal synthesis of niobium oxide using niobic acid in combination with oxalic acid in the same conditions as before. The obtained material showed a number of acid sites of 78 μmol g^{-1}, which is close to the value obtained for AO4h catalyst. Nevertheless, it is noteworthy that the differential of the materials reported in this work is the use of a more economically viable precursor.

3.2. Catalytic Tests

The synthesized catalysts were evaluated in fructose dehydration reaction aiming the formation of 5-HMF. The performance of several heterogeneous catalysts have been examined in this reaction, however, most studies use organic solvents or ionic liquid as the reaction medium.[36,37]

Thus, it was decided to use water as a solvent due to the significant advantages it offers compared to the solvents mentioned. Water is a green solvent, has high solubility for sugars and its disposal in the environment is generally not impactful. Although dehydration reactions in aqueous media may deactivate most solid acid catalysts, niobium-based materials have been presented water-tolerant acidic properties, which provide stability and has afforded good catalytic results.[38–40]

Figure 8 shows initial studies conducted in the presence of catalysts hydrothermally treated. For comparative purposes, Filter Cake, Filter Cake treated with neat water and the commercial niobic acid HY-340 (CBMM) calcined at 500ºC for 3 hours were also used as a control. As more significant result in the reaction conditions employed, 71% conversion and a yield of 22% for 5-HMF was obtained. This result is similar to that obtained by Wang et al.[41], who evaluated the catalytic performance of a series of porous niobium phosphate catalysts synthesized under hydrothermal conditions using CTAB as a template. The use of catalysts named NbPO-pH2 and NbPO-pH7 in fructose dehydration reactions carried out in aqueous medium at 130ºC for 60 minutes allowed to obtain conversions of 58 and 68% and yields of 45 and 34%, respectively.

As expected, in aqueous systems, dehydration of fructose is generally non-selective, leading to many byproducts besides 5-HMF. [42] Among the by-products identified by GC-MS the presence of furyl hydroxymethyl ketone, furfural, 1-(2-furanyl)-ethanone, 2,5-hexadione, 1-hydroxy-2-propanone and formic acid can be cited. It is noteworthy that although identified, such products have not been quantified. Therefore, the low yield observed in most of the reactions could be attributed to both the formation of these by-products as well as the formation of humins, as reported in the literature.[39]

We also observed a significant increase in conversion comparing the catalysts used as control (FC, FC hydrothermal, HY340) with those treated hydrothermally in the presence of oxalic acid and hydrogen peroxide. This demonstrates that the modifications imposed by the hydrothermal treatment described above exerted influence on catalysis.

It is very surprising that the AO4h catalyst showed the lowest conversion among those treated hydrothermally, despite it having high acidity and BET area. This result demonstrates that other characteristics of the catalyst play greater or equal influence on the studied reaction, such as morphology, effective acidity, mesoporosity and defects generated on the surface of catalyst. This way, it is not possible to associate the activity directly to just one of these variables.

In face of this initial results and in addition to characterization data that suggest the greater surface area of the AO4h catalyst and the presence of certain mesoporous feature for PH12h, it was decided to evaluate the effect that some factors have on the catalytic activity using these two materials in order to achieve optimization of reaction conditions.

3.2.1. Influence of fructose concentration

Comparing the data presented in Figure 9, it can be seen that the higher conversion values are obtained when using a lower sugar concentration (20g/L). Moreover, one can see that for higher fructose concentrations the HMF yield decreases slightly. This result is in agreement with reports in the literature.[6,43] It was also very surprising that at 60g/L the value of conversion was similar to the yield, leading to a selectivity close to 100%. At higher concentrations, the probability of rehydration to the formation of byproducts is reduced. Moreover, as the amount of available acid sites should have been insufficient to promote a higher conversion at 60g/L, the same reason may be associated with a reduction of secondary reactions for formation of humin and other byproducts.

3.2.2. Influence of the amount of catalyst

Increased catalyst mass exerted greater influence on the activity of FC and AO4h catalysts (Figure 10). On the other hand, there was a reduction in the yield of 5-HMF in the presence of higher catalyst loading.

The reason for obtaining a higher yield using a lower mass of catalyst may be associated with lower availability of acid sites that promote 5-HMF rehydration. In face of this result, the catalyst mass of 0.1g, fructose concentration of 20 g/L and the PH12h catalyst were chosen to continue the study of the other reaction variables.

It is noteworthy that although the AO4h catalyst presents higher acidity, it has not presented the best catalytic performance despite this feature being extremely important for reactions as studied here. The best results were obtained for the PH12h catalyst. This fact may be related to its mesoporous feature, which would facilitate the access of the substrate to the active site.

3.2.3. Temperature Influence

The results of fructose conversion and 5-HMF yield in function of the reaction temperature are shown in Table 3.

These results suggest that the reaction temperature is a crucial parameter for 5-HMF formation. The conversion increases from 6 to 71% by increasing the temperature from 70ºC to 130ºC, and there was no formation of 5-HMF at temperatures of 35 and 70ºC.

Kinetic studies show that the conversion of fructose into 5-HMF has an activation barrier of approximately 140 kJ/mol, in contrast to activation energy associated with undesirable side reactions (~ 60 kJ/mol).[44] Therefore, the 5-HMF yield tends to increase with a higher temperature, but its value is influenced by the nature of the reaction system, whereas in aqueous systems fructose dehydration is usually non-selective, leading to the formation of many by-products. In view of results presented, 130ºC was chosen as the optimum temperature reaction.

3.2.4. Influence of Reaction Time

As seen on Figure 11, the conversion increases with reaction time and reaches a plateau at the time of 2 hours.

Data in the literature has demonstrated that long reaction times contribute to the formation of by-products due to decomposition of 5-HMF in humins, levulinic acid, formic acid and other condensation products.[45] This explains, therefore, the low yield values obtained for reaction times longer than 3 hours.

Carlini *et al.*[13] using solid acid catalysts based on niobium (niobic acid and niobium phosphate) in an aqueous medium and at 100°C evaluated dehydration of fructose, sucrose and inulin aiming at the formation of 5-HMF. The results showed that shorter reaction times (30 minutes) give higher selectivities for 5-HMF (>90%) and low substrate conversion (about 30%). However, the increase in reaction time made possible the increase of sugar conversion (~ 60%) and reduced the 5-HMF selectivity.

To investigate further the 5-HMF formation, the reaction mixture was analyzed by NMR spectroscopy. Figure 12 shows the ^{1}H NMR spectrum for the dehydration fructose with PH12h in water after 2h at 130°C. The peaks between 3 and 4.5 are attributed to fructose, while the peaks at 8.35 and 9.45 are assigned to formic acid and 5-HMF, respectively.[46] The signal for the –COOH group proton of formic acid (H-1') was too small and some papers attribute that behavior to the fact that proton signal of formic acid did not resolve well in a reaction mixture or disappeared due to its consumption in undefined side reactions.[47]

It was also carried out ^{13}C NMR analysis (Figure 13) for the reaction and for 5-HMF standard. Such spectra confirmed the production of 5-HMF with the corresponding peaks identified as C-1 to C-6. As in the ^{1}H NMR spectrum, the presence of formic acid as side product was also evidenced, which can be explained by the rehydration of 5-HMF. Moreover, the self-polymerization of 5-HMF molecules or cross-polymerization of 5-HMF with fructose is also possible,[48] particularly due to the fact that the 5-HMF yield is not increased upon prolonged reaction as shown previously.

Under optimum reaction conditions, the stability of the catalyst was evaluated in subsequent reactions, given its importance. Figure 14 shows the results of four reuses. After each catalytic cycle, the PH12h catalyst was recovered by centrifugation, washed with water and dried at 100°C for 3h.

We can see, therefore, the successive deactivation of the catalyst. The literature has pointed out the formation of sugar-derived insoluble humin polymers and its deposition on the catalyst as the main cause of the deactivation.[49]

As previous research indicated that solvent plays a very important role in the reaction, dimethyl sulfoxide (DMSO) was used as solvent in the previously optimized conditions in order to evaluate its effect on the catalytic performance of the materials reported here.

As Figure 15a demonstrates, catalytic performance of the catalysts was noticeably affected by the solvent. Higher yields for 5-HMF are obtained in DMSO than in water. Fructose was almost completely converted over all the catalysts since it was not possible to observe its signal in ^{1}H NMR spectra (Figure 15b). Typical HMBC e HSQC spectra were also obtained for reaction using PH12h as catalyst and they are shown in supplementary information. The yield of 5-HMF reaches the maximum (47%) on the PH12h catalyst. Clearly, the catalysts in DMSO are also an effective system in promoting dehydration of fructose to 5-HMF. No rehydration byproducts such as levulinic acid and formic acid were detected.

Although there are no concrete and well-understood reasons, some studies have demonstrated what would be the contribution of these aprotic solvents for the dehydration reaction.

Previous studies have suggest that the use of DMSO as solvent increases the fructose conversion rate and decreases the rate of unwanted side reactions, thus resulting in higher selectivity. This aspect is attributed to the capacity of DMSO to associate with water molecules that are generated during dehydration, which prevents the reaction to proceed beyond 5-HMF to form FA and LA.[50]

Moreover, the higher conversion rate is related to the tautomeric equilibrium composition. In the presence of DMSO equilibrium towards a higher proportion of furanose forms. As such, a faster reaction could reduce the amount of condensation by-products generated through the reaction of 5-HMF with fructose or another intermediary.[51]

4. CONCLUSIONS

In summary, nanostructured niobium oxide was successfully hydrothermally synthesized with the use of oxalic acid and hydrogen peroxide under mild conditions. The hydrothermal synthesis along with structure-directing agents mentioned played an important role in the structure of the materials. It was possible to obtain nanoparticles with different morphologies. This synthesis method still promoted the modification of porous properties with increase in BET area and made possible the increase of acidity, which have significant influence on the type of reaction studied.

The obtained results demonstrate that the use of the new class of catalysts described in this study showed significant catalytic potential in fructose dehydration reaction in both aqueous medium and DMSO as solvent aiming to obtain 5-HMF. The use of PH12h catalyst afforded yields of up to 22% and 47% under optimal reaction conditions in aqueous medium and DMSO, respectively.

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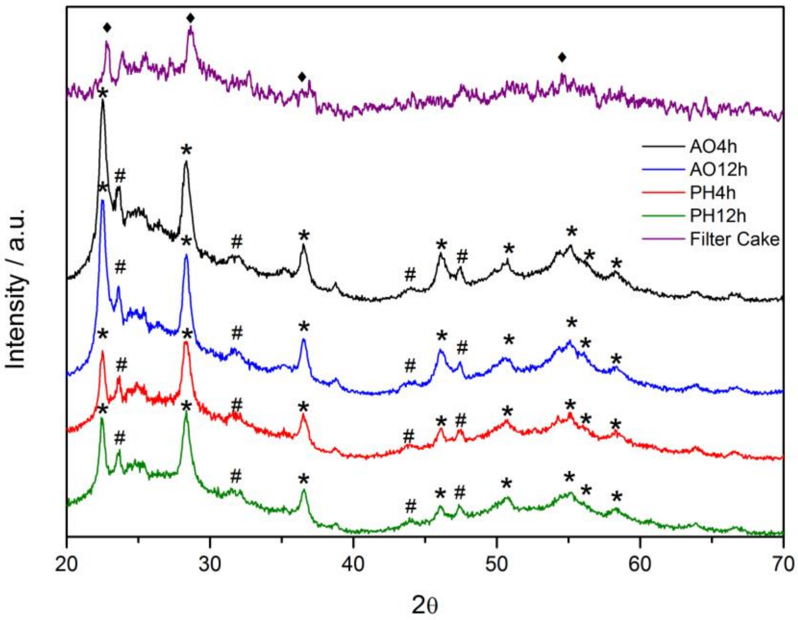


Figure 1. Diffraction patterns of X-ray of the catalysts synthesized (* = Nb_2O_5 (JCPDS - ICDD file 27-1312); # = $Nb_3O_7(OH)$ (JCPDS - ICDD file 31-928) ♦= Nb_2O_5(JCPDS - ICDD file 7-61)).

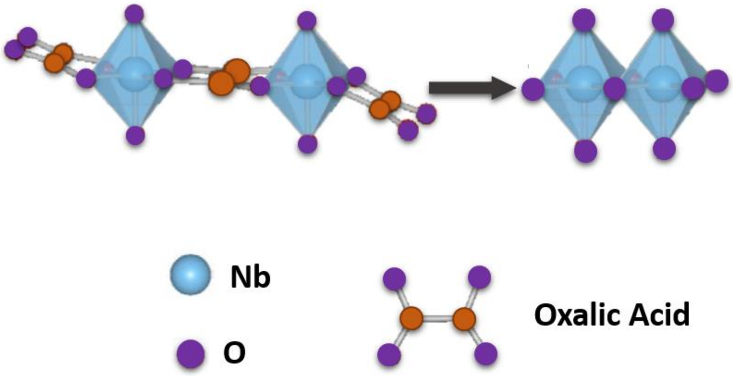


Figure 2: Scheme of a possible action mechanism of the oxalic acid. Adapted from TRUONG *et al.*[17]

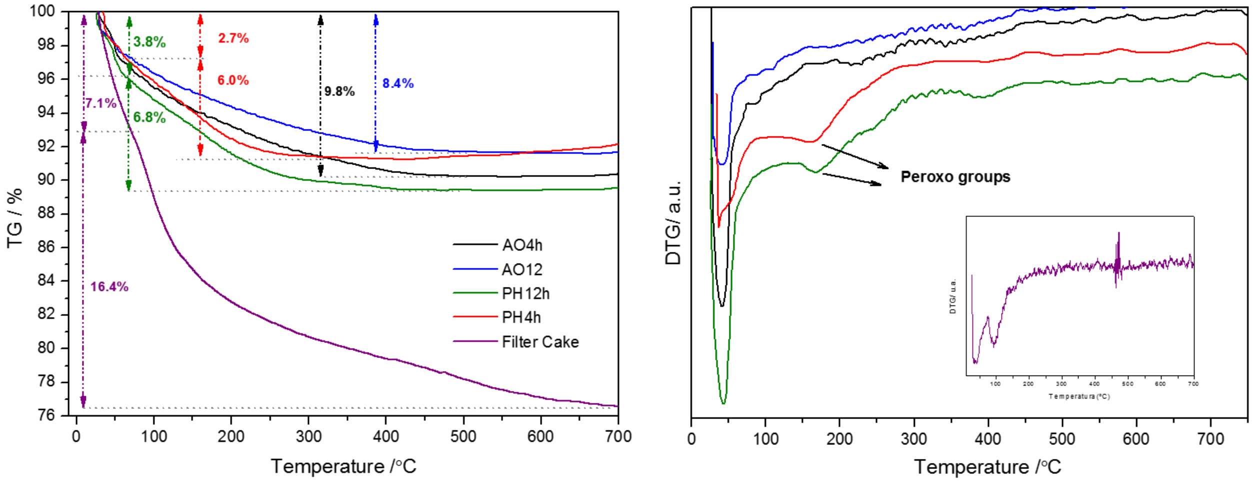


Figure 3. Thermogravimetric analyses in air atmosphere for catalysts based on niobium.

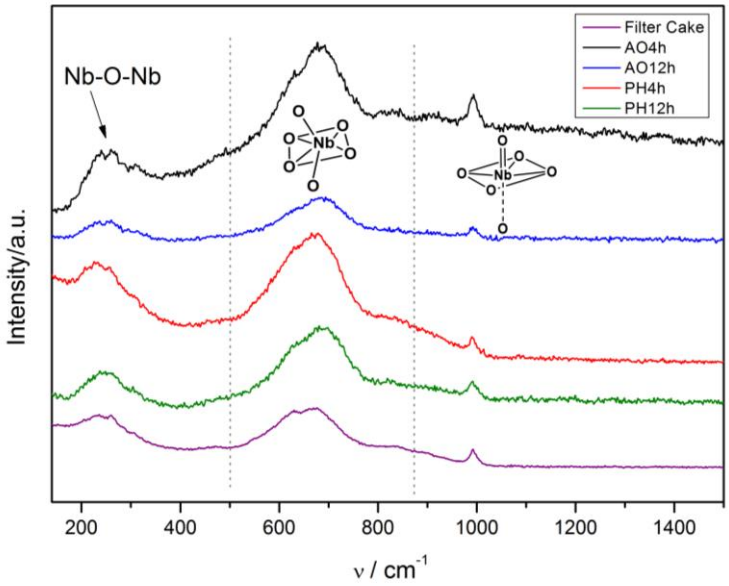


Figure 4. The Raman spectrum of the catalysts Filter Cake, AO4h, AO12h, PH4h and PH12h.

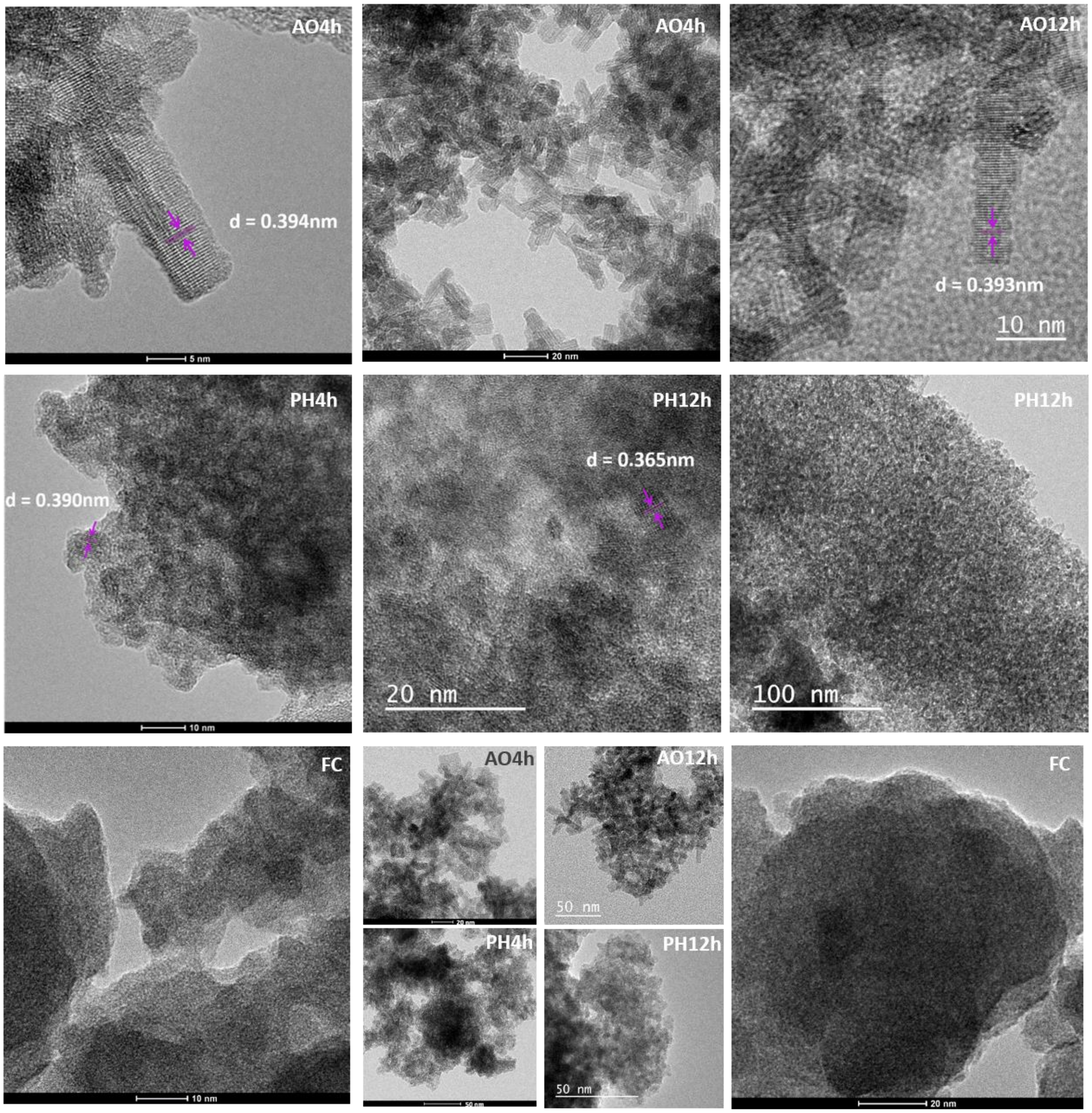
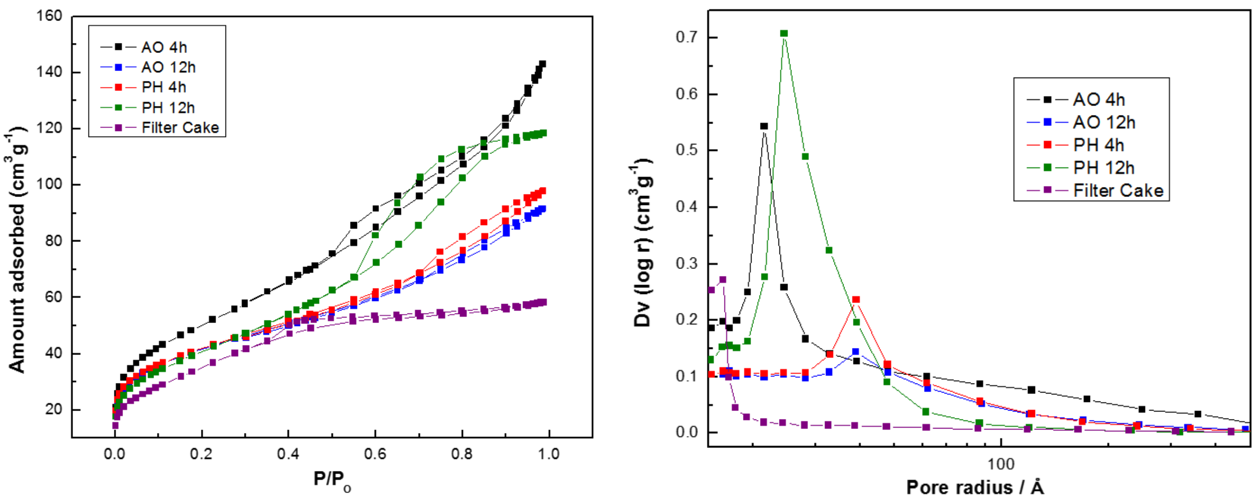


Figure 5. Images of transmission electron microscopy for the samples AO4h, AO12h, PH4h, PH12h and Filter Cake (FC).



(a) (b)

Figure 6. (a) N_2 adsorption/desorption isotherms and (b) the respective pore size distribution of catalysts.

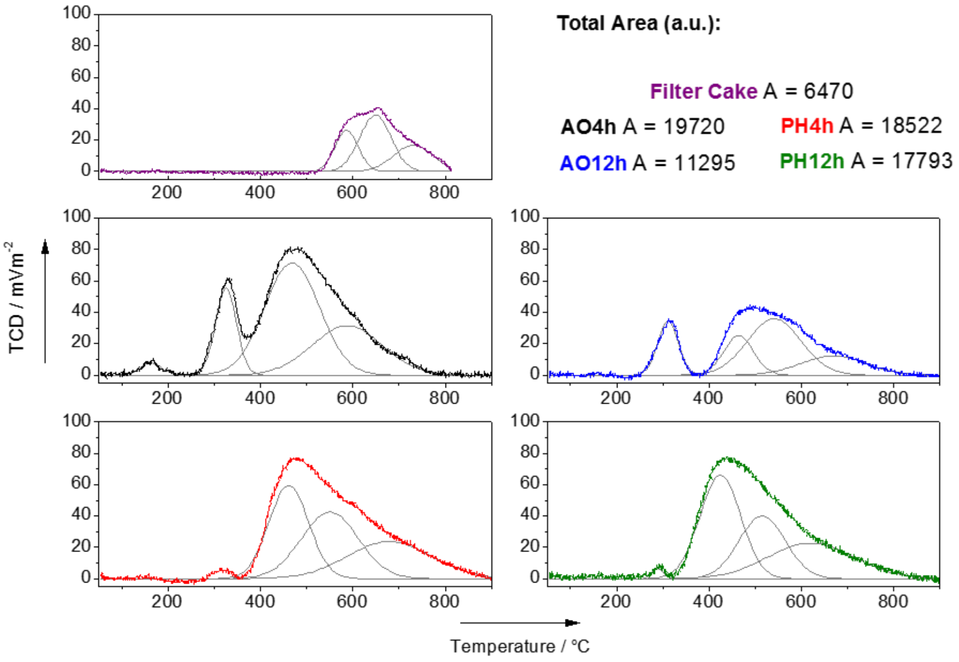


Figure 7. TPD-NH_3 profiles for Filter Cake and for catalysts synthesized hydrothermally. The number of acid sites was determined from the standard beta zeolite with a specified number of sites of 472 μmol g^{-1}.[32]

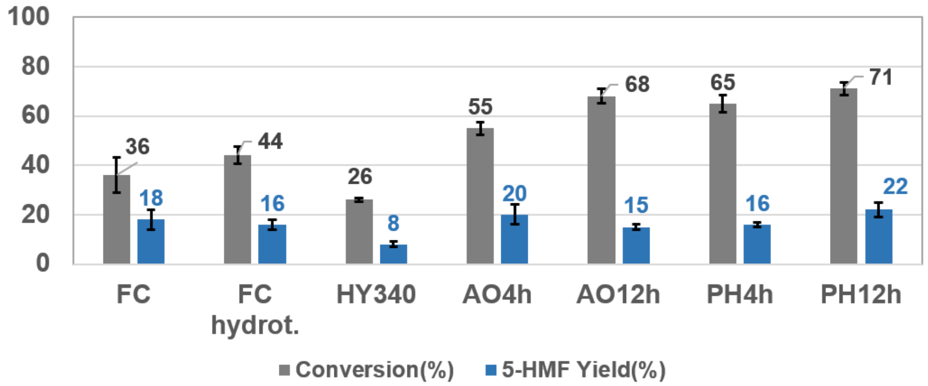


Figure 8. Fructose dehydration reactions in the presence of different catalysts. (Reaction conditions: 0.1g of catalyst, 130ºC, 2h, 20g/L of fructose).

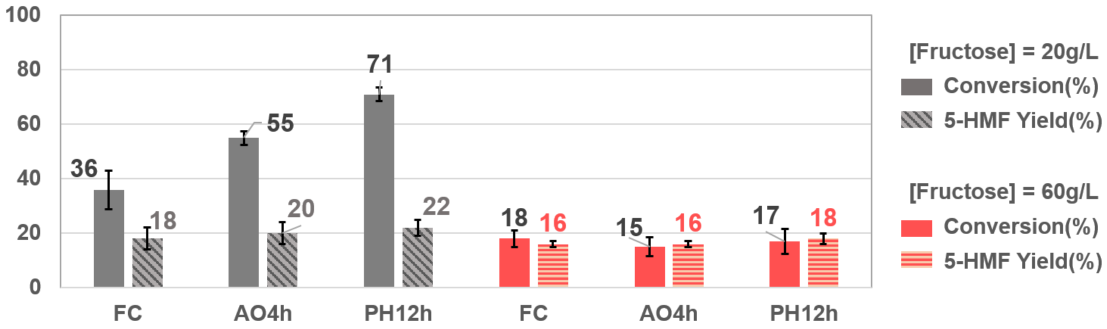


Figure 9. Influence of the fructose concentration on conversion and 5-HMF yield using a temperature of 130°C, reaction time of 2 hours and 0.1 g of catalyst.

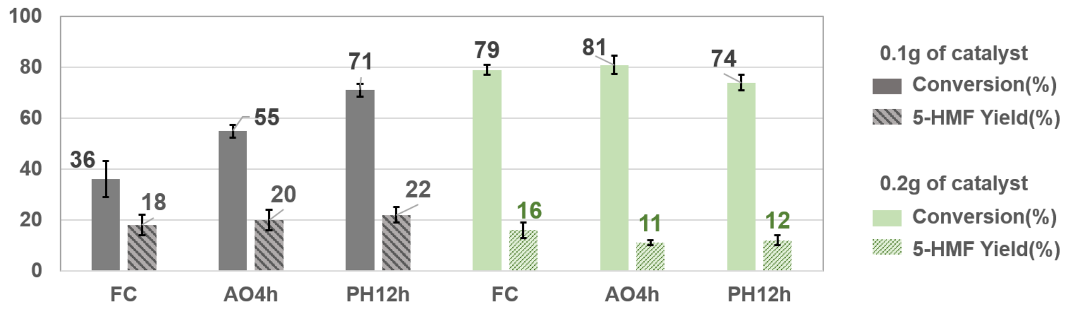


Figure 10. Influence of the catalyst mass on the fructose conversion and 5-HMF yield using a temperature of 130°C, reaction time of 2 hours and 20g/L of fructose.

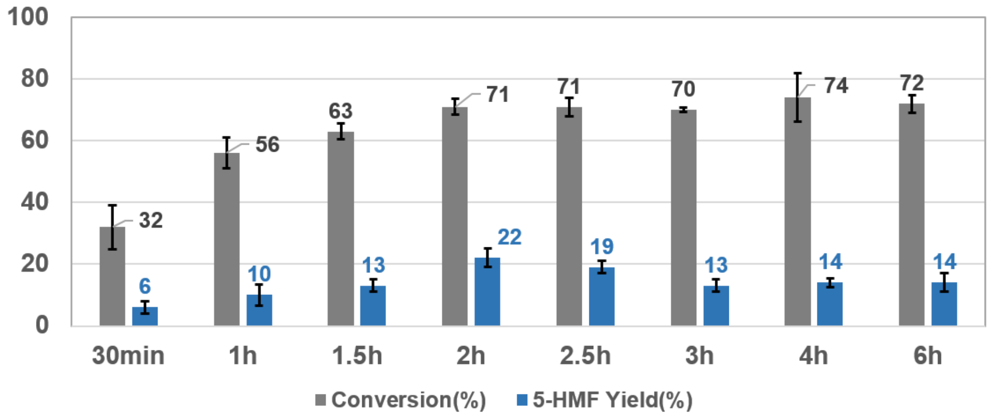


Figure 11. The influence of reaction time on fructose conversion and 5-HMF yield using a 130°C, sugar concentration of 20g/L and 0.1g of catalyst PH12h.

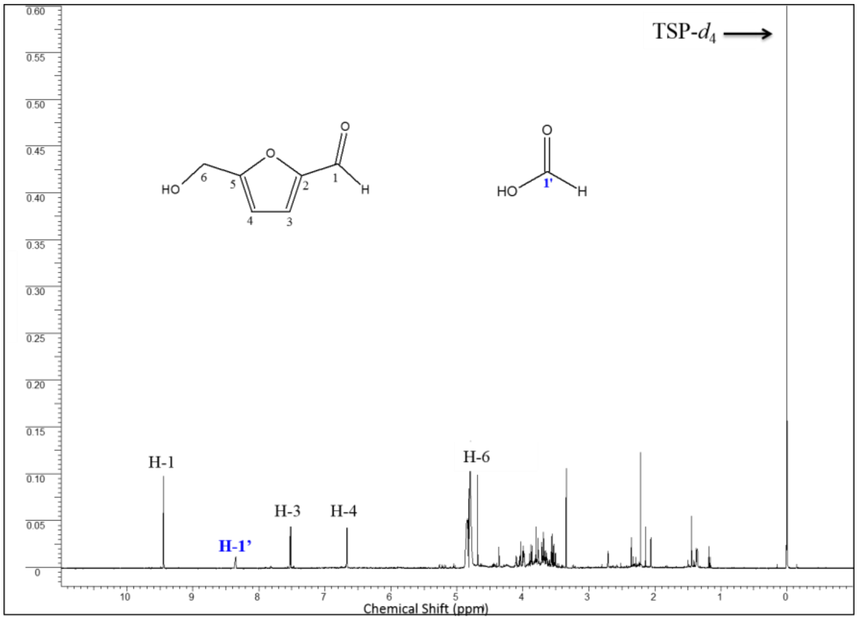


Figure 12. ^{1}H NMR spectrum of product obtained from dehydration reaction of fructose with PH12h in water after 2h at 130°C. (D_2O, 400 MHz). TSP-d_4 was used as an internal standard.

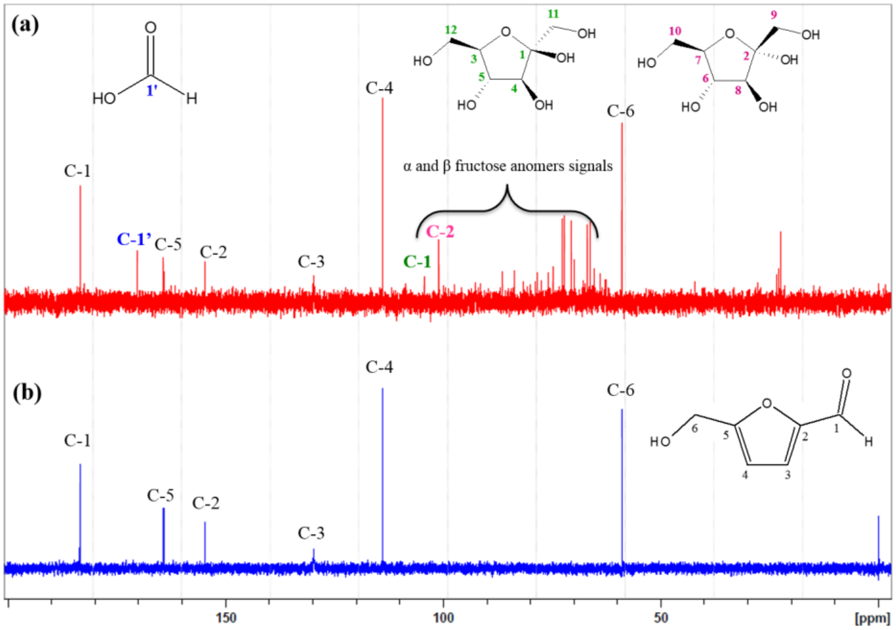


Figure 13. ^{13}C NMR spectra for (a) fructose dehydration reaction and (b) HMF standard as comparison. (D_2O, 400 MHz).

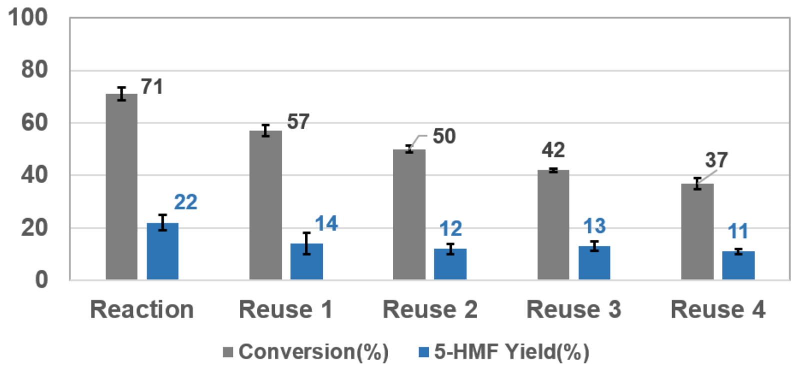


Figure. 2 Fructose conversion and 5-HMF yield using 130ºC, sugar concentration of 20g/L, 0.1g of PH12h catalyst.

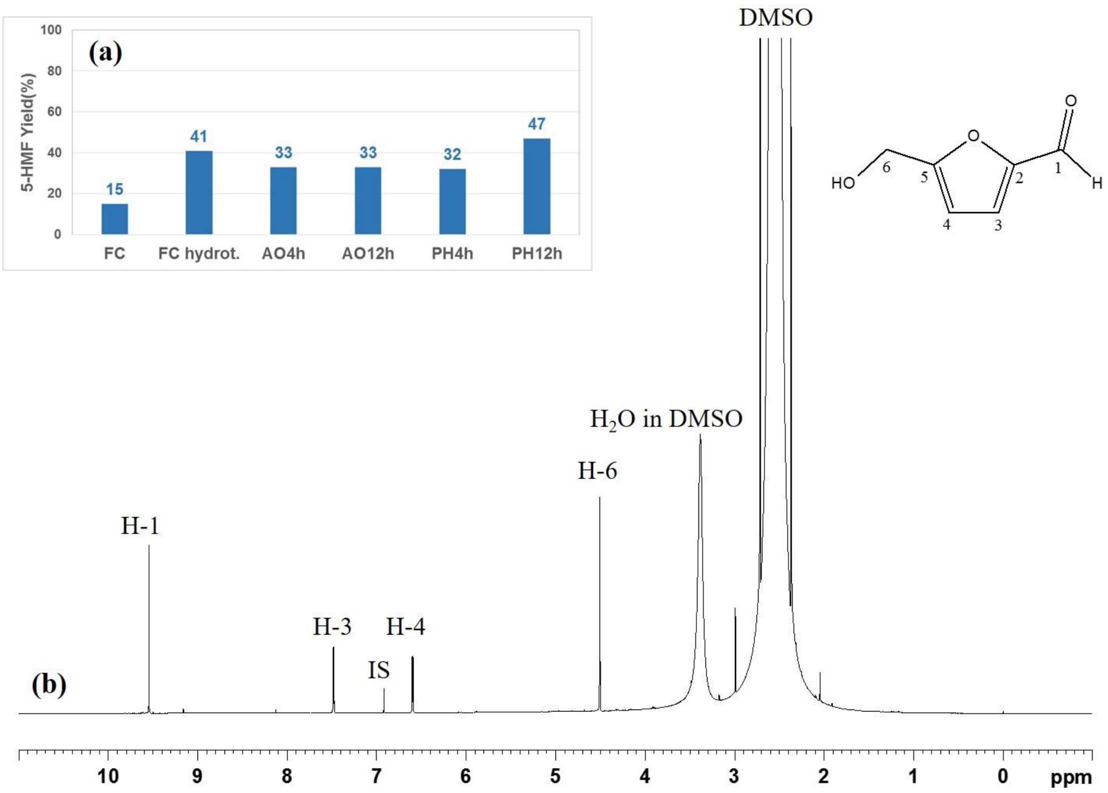


Figure 15. a) Effect of solvent on the yield of 5-HMF. (Reaction conditions in DMSO: 130ºC, 2h, 10mL of fructose in a concentration of 20g/L, 0.1g of catalyst). b) Typical proton ^{1}H NMR spectrum of reaction product using PH12h (DMSO-d_6, 400 MHz). IS* H-2,6 atoms signal of the internal standard gallic acid.

Table 1. Number of acid sites and textural properties of the catalysts.

Catalyst	Number of acid sites (μmol g^{-1})[a]	BET area (m^2g^{-1})	Total pore volume [cm^3g^{-1}]
FC	18	126	0.09
AO4h	58	182	0.22
AO12h	31	151	0.14
PH4h	51	151	0.15
PH12h	49	148	0.18

[a] Number of acid sites determined by TPD-NH_3 from the standard beta zeolite with a specified number of sites of 472 μmol g^{-1}.[32]

Table 3. Fructose dehydration reactions at different temperatures using 0.1g of the catalyst PH12h and 2 hours of reaction time.

Entry	[Fructose] g/L	Temperature (°C)	Conversion (%)	5-HMF Yield (%)
1	20	35	2	0
2	20	70	6	0
3	20	130	71	22