

Influence of Lewis acidity and CaCl₂ on the direct transformation of glucose to 5-hydroxymethylfurfural

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Abstract

Nb-Zr oxides were evaluated for glucose dehydration to 5-hydroxymethylfurfural. A linear relationship was found between the amount of acid sites and niobium content. Pure Nb₂O₅ showed the highest acid concentration and surface area and both Brönsted and Lewis acid sites, whereas Zr-containing catalysts mostly showed Lewis acid sites. Thus, a correlation between the amount of acid sites and catalytic performance was demonstrated, in the absence of metal salt, being Nb₂O₅ the most active catalyst. However, the catalytic results obtained by the combination of CaCl₂ and Zr-containing catalysts, which only showed Lewis acid sites, suggested the direct formation of HMF, without fructose formation, unlike that observed for Nb₂O₅, which possesses both Brönsted and Lewis acid sites. A HMF yield of 44 % was attained by using Nb₃Zr₇ as acid catalyst and CaCl₂ after 90 min at 175 °C. These catalysts can be reused at least 3 catalytic runs without any pretreatment.

Keywords: *5-hydroxymethylfurfural, glucose dehydration; calcium chloride; Lewis acid sites; solid acid catalysts.*

1. Introduction

Lignocellulosic biomass is currently considered as a promising alternative to fossil resources for the production of fuels and value-added chemicals, due to this is one of the most abundant renewable resources [1]. It is generally composed of 40-50% cellulose, 25-30% hemicellulose and 15-30% lignin, being carbohydrates the major component which can be transformed to relevant chemicals [2]. In this sense, through the hydrolysis of cellulose, glucose is easily obtained, which can be dehydrated to 5-hydroxymethylfurfural (HMF). HMF has been included in the list of top 10 value-added bio-based chemicals by the United States Department of Energy, being a versatile

precursor for valuable chemicals, such as 2,5-furandicarboxylic acid, 2,5-dimethylfuran, levulinic acid, 2-hydroxymethyltetrahydrofurfural, 2,5-hydroxymethyl furan, 2,5-hydroxymethyltetrahydrofuran, γ -valerolactone, among others [3-5]. The synthesis of HMF can be performed through the acid-catalyzed dehydration of hexoses, by elimination of three water molecules. Many studies about fructose dehydration into HMF have been reported in the literature [1, 6-9], but the utilization of glucose as feedstock is preferred due to its abundance and it is easily obtained from cellulose hydrolysis. In general, fructose is much more reactive than glucose and higher conversion and HMF selectivity values can be attained, because of glucose shows higher stability of ring structure [10, 11]. It has widely been reported that glucose dehydration requires two consecutive steps: i) isomerization of glucose to fructose catalyzed by basic or Lewis acid sites and ii) the dehydration of fructose into HMF catalyzed by Brönsted and Lewis acid sites [2]. Thus, a suitable balance of Lewis and Brönsted acid sites is a key factor to enhance the glucose dehydration into HMF [12, 13]. Although most of the work aimed at the production of HMF from C6 sugars has been carried out by conventional heating, novel and more advanced reaction systems, such as the use of microwaves, are receiving a lot of attention in recent years [14]. In last years, important efforts have been realized to achieve high HMF yields by using glucose as feedstock. Thus, different solid acid catalysts, such as zeolites [15-17], metal oxides [18-21], metal phosphates [22-24] and sulfated metal oxides [25-27] have been evaluated. It is well known that Nb_2O_5 is a water-tolerant solid and niobia-based catalysts mainly display Lewis acidity, although the presence of both Lewis and Brönsted acid sites has been detected for these materials [28-30]. In addition, niobium oxide has demonstrated to be active in the dehydration of several carbohydrates,

including glucose [6, 31-36]. Although several works have been published by using niobic acid for dehydration of glucose, low HMF selectivities were generally attained [21, 34-36]. Therefore, some authors have tried to improve its catalytic performance by a treatment with H_3PO_4 [31], or carrying out the synthesis of mesoporous Nb_2O_5 [30], thus enhancing HMF yield values. On the other hand, mixed metal oxides with a suitable Brønsted/Lewis acid ratio have also been proposed in the literature for glucose dehydration. Thus, several catalysts based on Nb_2O_5 and WO_3 with different Nb and W composition have been synthesized in order to control the Brønsted/Lewis acid sites ratio, which is a key point to achieve high HMF yields from glucose [13, 30, 37]. Thus, it is generally accepted that Lewis acid sites promoted the isomerization of glucose to fructose while Brønsted acid sites facilitated fructose dehydration to HMF.

Zirconium oxide has demonstrated to be active for glucose dehydration into HMF, even though it is essentially a Lewis acid solid [20, 38, 39]. However, Zhang et al. evaluated the influence of calcination temperature on the Brønsted/Lewis acid sites ratio for zirconia, in such a way that this ratio was maximum after calcination at 300 °C [40]. They tested these catalysts for dehydration of glucose into HMF, achieving almost full glucose conversion and a HMF selectivity about 40%. Therefore, both Nb_2O_5 and ZrO_2 demonstrated to be active for dehydration of glucose by themselves. On the other hand, Stošić et al. synthesized mesoporous $\text{Nb}_2\text{O}_5\text{-MeO}_2$ mixed oxides, among them $\text{Nb}_2\text{O}_5\text{-ZrO}_2$, and evaluated their catalytic performance for fructose dehydration into HMF. They proved that the amount of strong acid sites influenced on both the activity and selectivity, but, although Nb_2O_5 and $\text{Nb}_2\text{O}_5\text{-ZrO}_2$ catalysts displayed similar acid sites concentration, the presence of zirconium did not improve the catalytic performance with respect to pure Nb_2O_5 [41]. However, they did not study the influence of the

ZrO₂/Nb₂O₅ molar ratio on the catalytic performance and, moreover, these catalysts were only tested for fructose dehydration, which is considered more favorable than from glucose. Considering that dehydration of glucose generally requires Lewis acid sites, or basic sites, for the isomerization of glucose to fructose, before its dehydration to HMF, and ZrO₂ exhibits essentially Lewis acidity, the addition of different amounts of ZrO₂ to Nb₂O₅ could be of great interest for HMF production. Likewise, Gromov et al. [38] prepared different acid solid based on Nb₂O₅ supported on ZrO₂ (0-2.8 wt% Nb) for the transformation of cellulose to glucose and HMF. The incorporation of niobium species generated Brønsted acid sites associated to polymeric NbO_x species, thus increasing the catalytic activity of Nb₂O₅-ZrO₂. The highest HMF yield (16%) was attained with the 2.8%Nb/ZrO₂ catalyst.

On the other hand, the existence of side reactions involving HMF leads to the formation of humins and other soluble and insoluble polymers, as well as HMF rehydration yielding levulinic and formic acids [9, 42, 43]. In order to minimize these undesired reactions, different methods have been proposed, as the use of co-solvents to extract HMF after its formation [9, 42, 43], or the addition of inorganic salts, to improve the partition coefficient. The salting-out effect does not seem to be clear in the literature, since some authors justify the improvement of yield to the effect of anions [44] or cations [45]. It has been also reported that alkaline earth metal salts provided higher HMF yields than alkaline ones, because Ca²⁺ and Mg²⁺ cations promoted glucose conversion [46]. In a previous study, it was reported that the presence of CaCl₂ notably enhanced the catalytic performance due to the Ca²⁺ cations favored the formation of α-D-glucopyranose, achieving values of glucose conversion and HMF yield of 96% and 52%, respectively, at 175 °C after 15 min in the presence of CaCl₂ and γ-Al₂O₃ [47].

Thus, calcium cations promoted the formation of α anomer and alumina accelerated the dehydration process, providing a high HMF yield at short reaction times, by using glucose as feedstock. However, this effect was only evaluated in the presence of alumina as solid acid catalyst, in such a way that it was not possible to know if there was a relationship between the presence of CaCl_2 and the type of acid sites existing in the catalyst.

The main goal of this work was to deepen about the effect of CaCl_2 in the presence of solid acid catalysts based on Nb_2O_5 and ZrO_2 phases, with Lewis and/or Brönsted acid sites. Considering that ZrO_2 usually provides strong Lewis acid sites, this could accelerate the isomerization of glucose to fructose, facilitating its subsequent dehydration into HMF. Thus, the synthesis of mesoporous Nb-Zr oxides to evaluate their catalytic activity in the dehydration of glucose into HMF in a biphasic water–methyl isobutyl ketone (MIBK) solvent system was carried out. These catalysts were characterized by several physico-chemical techniques in order to establish a suitable correlation between properties and catalytic performance, primarily textural and acidic properties. The effect of different experimental parameters, such as temperature and time reaction, and the addition of CaCl_2 , on the catalytic performance was studied, as well as their reusability. Likewise, the influence of adding this inorganic salt, in the presence of Lewis and Brönsted acid sites associated to Zr and Nb species, on the pathway followed for HMF production was also evaluated in order to know if there is a relationship between the use of this salt and the type of acid sites involved for this reaction.

2. Experimental

2.1. Reagents

Mesoporous niobium and zirconium oxides were synthesized using NbCl_5 (Sigma-Aldrich, 99%) and ZrCl_4 (Sigma-Aldrich, >99.5%) as precursor salts, Pluronic P-123 (Mn~ 5800 Da, Aldrich) as surfactant and n-propanol as solvent (GPR Rectapur, 99%).

The following chemicals were utilized for the catalytic tests: glucose (Sigma-Aldrich, >99%), fructose (Sigma-Aldrich, >99%) and calcium chloride (VWR, 97%). Deionized water and MIBK (VWR, 98%) were used as solvents.

2.2. Catalyst preparation

Mesoporous metal oxides were synthesized by using a similar neutral templating route to that previously reported by Tagusagawa et al. for Nb-W oxides [48]. Thus, 7 mmol of XCl_y (NbCl_5 and/or ZrCl_4) were incorporated to a template solution previously formed by dissolving 1 g of P-123 in 10 g of n-propanol. After vigorous stirring for 5 min, 0.54 g of water were added to the mixture at room temperature, maintaining the stirring for 30 min. The solution was aged at 40 °C for 10 days. The structure-directing agent was removed by calcination in air at 450 °C for 6 h (1 °C·min⁻¹). The pure metal oxides were denominated by their chemical formulas (Nb_2O_5 and ZrO_2) and the mixed metal oxides were labeled as Nb_xZr_y , where x and y indicated mol of Nb and Zr, respectively, in the synthesis solution.

2.3. Catalyst characterization

Powder X-ray diffraction patterns were collected on a PANalytical automated diffractometer, EMPYREAN model, using $\text{Cu-K}\alpha_{1,2}$ (1.5406 Å) radiation and a last generation PIXcel detector.

Textural parameters were measured by N_2 adsorption–desorption at -196 °C, determined by using an automatic ASAP 2420 model of gas adsorption analyser from

Micromeritics. Prior to nitrogen adsorption, samples were degassed at 200 °C and 10^{-4} mbar for 10 h. Surface areas were calculated by using the Brunauer–Emmet–Teller (BET) equation and taking a value of 16.2 \AA^2 for the cross section of the adsorbed nitrogen molecule at -196 °C. Pore size distributions and average pore size were determined with the BJH method by using the desorption branch.

Raman spectra were recorded on a Raman Senterra (Bruker) microspectrometer, equipped with a thermoelectrically cooled charge coupled device (CCD) detector. A Nd:YAG laser was used as the excitation source at 532 nm and the laser power was set to 5 mW. Raman spectroscopy was performed on powder samples without any previous treatment by averaging spectra during 60-90 min, with a resolution of $3\text{--}5 \text{ cm}^{-1}$. A CCD camera operating at $-50 \text{ }^\circ\text{C}$ was used for the Raman detection.

X-ray photoelectron spectroscopy (XPS) studies were performed with a PHI Versaprobe II spectrometer with a high flux X-ray source providing a non-monochromatic Mg $K\alpha$ radiation (300 W, 15 kV and 1253.6 eV). High-resolution spectra were recorded at a given take-off angle of 45° by concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV. Charge referencing was measured against adventitious carbon (C $1s$ at 284.8 eV). A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine binding energies of different element core levels more accurately.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was performed to evaluate the total surface concentration of acid sites for catalysts. After cleaning the catalyst (0.08 g) with helium up to calcination temperature, 450 °C, and subsequent adsorption of ammonia at 100 °C, the NH_3 -TPD was performed by raising the

temperature from 100 to 450 °C, under a helium flow of 40 mL min⁻¹, with a heating rate of 10 °C min⁻¹. The evolved ammonia was analyzed by using a thermal conductivity detector (TCD) of a gas chromatograph (Shimadzu GC-14A).

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to study the type (Lewis and Brönsted) and strength of acid sites present in catalysts. Analyses were carried out by using a VERTEX 70 spectrometer coupled with an external sample chamber that enables measurements under vacuum (Bruker, Germany). Catalysts were diluted with KBr prior to the analysis (~5 wt.% of sample), and dried in situ under vacuum ($<2 \cdot 10^{-2}$ mbar), either at room temperature for 1 h prior recording the background spectra. Then, the catalyst was put in direct contact with pyridine vapours at 40 °C for 5 min. The main spectral features were recorded from 1700 to 1400 cm⁻¹ range, 200 scans, and a resolution of 4 cm⁻¹. The pyridine desorption was followed by heating the sample under vacuum up to 125, 175 or 225 °C for 15 min and recording a spectrum after cooling the sample at room temperature.

2.4. Catalytic tests

Glucose dehydration catalytic tests were carried out in batch reactors at different temperatures by using a glass pressure tube with thread bushing (Ace, 15 mL, pressure rated to 10 bars) and magnetic stirring. In a typical experiment, 0.15 g of glucose, 0.05 g of catalyst, 1.5 mL of deionized water and 3.5 mL of MIBK were poured into the reactor. For those catalytic test in presence of CaCl₂, 0.65 g CaCl₂ per g aqueous solution were dissolved in the aqueous solution together with glucose. This concentration had been optimized by our research group in a previous work [51]. Prior the experiments, reactors were always purged with nitrogen in order to avoid possible

undesired reactions. The reaction mixture was heated with a thermostatically controlled oil bath. The reaction was quenched by submerging the reactor in a cool water bath; the liquid phases were separated, filtered and the analysis of products was performed in both phases by high performance liquid chromatography (HPLC), being glucose, fructose and HMF the only detected products. A JASCO instrument equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055), column oven (co-2065) using a Phenomenex Luna C18 reversed-phase column (250 mm × 4.6 mm, 5 μm) and Phenomenex Rezex RCM-Monosaccharide Ca²⁺ (8%) (300 mm × 7.8 mm, 5 μm), was employed. Both glucose and fructose were monitored using a refractive index detector for aqueous phase, while HMF production was monitored using a UV detector in both phases. The mobile phases consisted in pure methanol (flow rate 0.5 mL·min⁻¹) for Luna C18 and deionized water (flow rate 0.6 mL·min⁻¹) for Rezex RCM-Monosaccharide, being the columns at room temperature and 80 °C, respectively.

Glucose conversion, selectivity and yield for fructose and HMF were calculated by the next equations, considering HMF recovered in both phases, aqueous and organic phases:

$$Conversion (\%) = \frac{\mu mol_{initial\ glucose} - \mu mol_{final\ glucose}}{\mu mol_{initial\ glucose}} \times 100$$

$$Selectivity_i (\%) = \frac{\mu mol_i\ produced}{\mu mol_{initial\ glucose} - \mu mol_{final\ glucose}} \times 100$$

$$Yield_i (\%) = \frac{Conversion \times Selectivity_i}{100}$$

3. Results and discussion

3.1. Characterization of catalysts

The X-ray diffraction technique was employed in order to determine the presence of crystalline phases in these catalysts, as well as their structural ordering. Figure 1A shows the XRD pattern in the low angle region, where an intense peak at $2\theta = 1.05^\circ$ was observed for Nb_2O_5 catalyst, corresponding to the d_{100} diffraction signal (8.4 nm), thus corroborating its mesoporous character, which agrees with other mesoporous niobium oxides reported in the literature [31, 48]. However, the absence of other well-defined diffraction peaks in the low-angle region would point out the lack of long-range order, probably due to the amorphous nature of its pore walls. This peak almost disappeared after zirconium incorporation to the catalysts, indicating that the presence of Zr could provoke the structural collapse. At the same time, new diffraction peaks emerged in the high-angle region (at $2\theta = 30.2$ and 50.2°) for Nb_xZr_y catalysts attributed to tetragonal zirconium oxide, which were more intense for ZrO_2 (PDF 01-079-1769) (Figure 1B). This fact agrees with that found by Zhang et al., who detected tetragonal zirconia for calcination temperatures around 400°C [40] and Stošić et al. [41], who detected the coexistence of amorphous mesoporous phase and ZrO_2 crystalline phase for mesoporous $\text{Nb}_2\text{O}_5\text{-ZrO}_2$ catalysts. However, crystalline Nb_2O_5 phases were not detected in any case, demonstrating the amorphous nature of niobia. These results are in agreement with those reported by Tagusagawa et al. for mesoporous Nb-W oxides, since they observed that the intensity of d_{100} diffraction peak decreased after W incorporation, and concomitantly crystallized WO_3 was detected in W-rich samples [48]. Therefore, it can be concluded that the mesoporous character of these mixed metal oxides decreased after Zr incorporation, increasing their crystallinity.

Textural properties were evaluated by N₂ sorption at -196 °C (Table 1). All adsorption-desorption isotherms were of Type IV according to the IUPAC classification, characteristic of mesoporous solids (Figure 2A). It can be observed that the incorporation of Zr to mesoporous Nb₂O₅ modified the mesoporous structure, according to XRD data. Thus, Nb₂O₅ exhibited a H2-type hysteresis loop, which is associated to mesoporous solid with non-uniform size or shape pores; however, the hysteresis loop tended to H4-type for high Zr contents, where the adsorption branch is more pronounced at low relative pressures, being associated with the filling of micropores [49, 50]. The hysteresis loop was shifted toward higher relative pressures for high Nb contents, indicating the existence of larger pores. The BJH pore size distribution revealed the presence of different pore sizes (2.5-9 nm) for Nb₂O₅, which became narrower after Zr incorporation and shifted at smaller pore sizes (2-5 nm) (Figure 2B). This fact was confirmed by the average pore sizes, which decreased for Zr-containing catalysts (Table 1) from 4.8 to 3.2 nm, as happened for mesoporous mixed Nb-W oxides with increasing W content [48]. Regarding the BET surface area and pore volume, their values decreased after addition of zirconium (from 150 to 104 m² g⁻¹ and from 0.213 to 0.101 cm³ g⁻¹, respectively), mainly when Zr mol was higher than Nb mol. These results corroborate XRD data, since Nb₂O₅ showed a higher long-range order and the crystallinity increased for high Zr contents, subsequently decreasing their specific surface area.

Raman spectra of different Nb_xZr_y oxides were also collected, although the signal was distorted after Zr incorporation (Figure 1SA), most likely due to fluorescence caused by 532 nm laser interaction with zirconia-niobia catalysts [51]. Therefore, no clear bands could be detected. However, the enlarged spectrum of Nb₂O₅ (Figure 1SB)

was similar to that found for other mesoporous niobium oxides previously reported [31, 41]. Thus, a well-defined peak was observed at 660 cm^{-1} , attributed to the vibrations of Nb - O - Nb bridges of slightly distorted octahedral NbO_6 connected sharing corners, which are associated with Brønsted acid sites. Likewise, a shoulder could be detected about 880 cm^{-1} assigned to the symmetric stretching mode of surface Nb=O species of highly distorted octahedral NbO_6 structures, related to Lewis acid sites [52]. The vibrational band expected at 988 cm^{-1} , associated to tetrahedral NbO_4 , was almost undetected; however, the decrease of intensity for this band had been observed in the presence of water, since $\text{NbO}_4\text{-H}_2\text{O}$ adducts would be immediately formed [53]. Another band centered at 235 cm^{-1} was also found for this sample, arising from the symmetric stretching mode of polyhedral niobia and the bending modes of Nb - O - Nb linkages. These bands were slightly discernible for Nb_7Zr_3 , mainly the peak at 660 cm^{-1} , but disappear for increasing Zr content. Tetragonal ZrO_2 phase was not detected by Raman spectroscopy for Nb_xZr_y and ZrO_2 , since their main signals at 272 and 647 cm^{-1} [54, 55] were not observed, perhaps due to low quality of these spectra and possible overlapping with bands corresponding to Nb_2O_5 .

X-ray photoelectron spectroscopy is a powerful tool to characterize the surface nature of solids. Binding energy values (Table 1S) of the photoelectron Nb $3d_{5/2}$ peak varied between 206.8 and 207.0 eV , which were in the typical range of Nb(V) in an oxidic environment [31, 37]. With regard to the Zr $3d$ core level, the binding energies ($181.9\text{-}182.7\text{ eV}$) can be assigned to Zr^{4+} in ZrO_2 [56]. It should be noted that ZrO_2 displayed a value of binding energy equal to 182.7 eV which slightly decreased for mixed metal oxides, mainly in the case of Nb_3Zr_7 (181.9 eV). This fact could be due to the presence of oxygen vacancies in the crystalline structure of ZrO_2 , as previously

reported by other authors [57, 58]. The photoelectronic peak of the O 1s core level was asymmetric and can be deconvoluted into two contributions: 529.7–530.6 and 531.7–532.6 eV. The former BE values related to oxide species could be attributed to ZrO₂ and Nb₂O₅, not being possible to differentiate them [31, 57, 59]. The higher BE contribution of the O 1s could coincide with values found in the literature for O 1s attributed to hydroxyl or carbonate species [60]. This was probably due to the formation of carbonates, since the C 1s core level spectra exhibited a contribution located about 288.4–288.9 eV, together with the adventitious carbon at ca. 284.8 eV [61]. On the other hand, the superficial Nb/Zr atomic ratio values were close to the bulk ones of mixed Nb-Zr oxides (Table 1S), confirming the homogeneous distribution of Nb and Zr species in the mixed metal oxides. This assumption was corroborated from the similar (Zr+Nb)/O ratio determined by XPS.

The number and strength of the acid centers were evaluated by NH₃-TPD analysis. The total concentration of acid sites is collected in Table 1 and the NH₃-TPD curves are depicted in Figure 3A. It is observed that the amount of acid sites decreased when the Zr amount increases; thus, the acidity values decreased from 411 μmol NH₃·g⁻¹ for Nb₂O₅ to 115 μmol NH₃·g⁻¹ for ZrO₂. This fact could be related to textural properties of these catalysts, in such a way that high niobia concentrations provided larger specific surface area and lower crystallinity, facilitating the access of NH₃ molecules to acid sites. Moreover, the starting of NH₃ desorption was slightly shifted at higher temperatures when the Zr molar content was equal or higher than the Nb one, showing that these catalysts possess a lower amount of weak acid sites. Therefore, the presence of zirconium provoked that the total amount of acid sites decreased mainly affecting to weaker acid sites. On the other hand, a relationship between total

concentration of acid sites and the metal concentration can be established (Figure 3B). Thus, the amount of acid sites linearly enhanced when the niobium concentration increased in catalysts, and accordingly pure niobia showed the greatest acidity. On the contrary, this concentration of acid sites decreased for increasing Zr contents.

In addition to total amount of acid sites, a key factor in the dehydration of glucose is the type of acid sites on the catalyst surface, since Lewis acid sites are required for the isomerization of glucose to fructose and Brønsted acid sites take part in dehydration of fructose into HMF. The presence of Lewis and/or Brønsted acid sites was elucidated by adsorption of pyridine coupled to FTIR spectroscopy, evacuating pyridine at different temperatures (125, 175 and 225 °C) (Figure 4). All the catalysts showed two bands at 1608 and 1444 cm^{-1} which were attributed to the 8a and 19b vibration modes of pyridine coordinated to strong Lewis acid sites (s-L), respectively [62]. These acid sites showed a high strength due to they were detected even after outgassing at 225 °C, although the intensity decreased as expected. In the case of ZrO_2 catalyst, these bands were less intense, demonstrating that this catalyst possesses a lower concentration of Lewis acid sites. Another band located at 1573 cm^{-1} was found mainly for Nb_2O_5 , which could be attributed to pyridine coordinated to weak Lewis acid sites (w-L) [62]. Moreover, this signal was less intense for higher outgassing temperatures, confirming their weakness. However, this band was barely observed for Nb_xZr_y catalysts, confirming NH_3 -TPD data, indicating that these mixed metal oxides displayed a lower proportion of weak acid sites than pure niobia. Likewise, Nb_2O_5 catalyst exhibited other two bands about 1637 and 1540 cm^{-1} which could be associated to the 8a and 19b vibration modes of pyridine coordinated to Brønsted acid sites [63]. These latter bands were maintained after evacuation at higher temperatures. Therefore,

niobium oxide possesses both Lewis and Brönsted acid sites, as recently reported [64]. However, the behavior of these latter bands was different for Zr-containing catalysts. They were found for Nb₇Zr₃, but their intensity seemed to increase with the outgassing temperature. In the case of Nb₅Zr₅, Nb₃Zr₇ and ZrO₂ catalysts, the appearance was different and two small bands were detected about 1550 and 1530 cm⁻¹ whose intensity also grew with the evacuation temperature. It has been proposed in the literature that these bands could be produced by oxidative breakdown of pyridine on strong Lewis acid sites giving rise to carbonaceous species [65]. As the band at 1637 cm⁻¹ was not detected for Nb₅Zr₅, Nb₃Zr₇ and ZrO₂ catalysts, the existence of Brönsted acid sites would be less likely. This fact agrees with results reported by Santos et al., who only found Lewis acid sites for ZrO₂ phase [64]. However, Brönsted acid sites could be generated in the aqueous reaction medium by the interaction of Lewis acid sites with water molecules [66]. On the other hand, in all cases, a band located at 1487 cm⁻¹ related to the 19a vibration mode of pyridine interacting with both Brönsted and Lewis acid sites was detected. Finally, a band at 1586 cm⁻¹ could be slightly perceived for Nb₃Zr₇, which could be attributed to the 8a vibration mode of pyridine bonded to the hydroxyl groups of catalyst by hydrogen bonds [67], but its intensity was almost insignificant. Therefore, Nb₂O₅ possesses both Brönsted and Lewis acid sites, whereas Zr-containing catalysts mostly showed Lewis acid sites. Unfortunately, the concentration of both types of acid sites could not be quantified due to the analytical procedure of acquiring the spectra, being able to affirm only that the Nb-rich catalysts provided the most intense bands ascribed to the Brönsted acid sites.

3.2. Activity in glucose dehydration to 5-hydroxymethylfurfural

It is well known that glucose dehydration requires the presence of Lewis and Brønsted acid sites in order to catalyze the isomerization of glucose to fructose and the dehydration of fructose into HMF, respectively [3]. However, the HMF yield could decrease due to the formation of soluble/insoluble polymers and/or humins by side reactions. In order to minimize the formation of these by-products, different alternatives have been proposed, such as the use of a biphasic system to extract HMF from the aqueous phase, immediately after its formation, being MIBK the most common organic co-solvent employed [68, 69]. In the present catalytic study, a biphasic water–MIBK system was used to improve the dehydration of glucose to HMF, with a partition coefficient ((HMF concentration in MIBK)/(HMF concentration in water)) of 1.1-2.0 for HMF.

Firstly, the effect of reaction was evaluated at 175 °C (Figure 5A). In all cases, both glucose conversion and HMF yield enhanced with the reaction time, maintaining almost stable values from 90 min, thus demonstrating the effectiveness of the biphasic water:MIBK system to avoid side reactions. Nb₂O₅ catalyst provided the highest glucose conversion and HMF yield values (90 and 36%, respectively) at 175 °C, after 90 min. This fact could be due to this catalyst displayed the highest total concentration of acid sites and the presence of an adequate Lewis/Brønsted ratio (Table 1 and Figure 4). This HMF yield was similar to those reported with other mesoporous niobium oxide from fructose dehydration [41] and glucose dehydration from more diluted solutions [30], being higher than those observed for niobic acid [21,34-35]. However, both glucose conversion and HMF yield decreased when the Zr content increased for Nb_xZr_y catalysts (79 and 30%, respectively, for Nb₅Zr₅, after 90 min at 175 °C), being close to the value attained by Stošić et al. with a Nb₂O₅-ZrO₂ catalyst in fructose dehydration in

spite of the glucose dehydration is more difficult than fructose [41]. Therefore, these catalysts prepared in the present work were able to provide comparable HMF yields from glucose, whose dehydration possesses more interest than the fructose one. Likewise, the catalytic performance was better than that reached by Gromov et al. from glucose dehydration after 3 h at 180 °C in the presence of an acidic NbO_x/ZrO₂ catalyst, under 1 MPa of argon, who attained glucose conversion and HMF yield values of 84.3 and 22.6%, respectively [38]. It can be observed that the lowest conversion and HMF yield (42 and 14%, respectively) were found for ZrO₂, after 120 min at 175 °C (Figure 5A). Similar catalytic results were found by Zhang et al. for glucose dehydration with zirconia [70]. Therefore, it is clear that the incorporation of niobium considerably improved the catalytic performance of these mixed metal oxides. In order to deepen about the influence of the total amount of acid sites, the catalytic performance was evaluated at short reaction time (30 min), to minimize the influence of side reactions, and represented as a function of total concentration of acid sites for catalysts (Figure 5B). A clear linear relationship was observed between both conversion and HMF yield values and total amount of acid sites, which in turn is closely related to the niobium concentration. Thus, it could be confirmed that the concentration of acid sites is a key factor for HMF production from glucose. Moreover, these values of total acidity did not distinguish between Lewis and Brønsted acid sites, although certainly a higher Nb concentration implies a greater amount of Brønsted acid sites as was detected by pyridine adsorption coupled to FTIR spectroscopy. Therefore, it would be feasible that the presence of Brønsted acid sites would influence on the catalytic performance, favoring the HMF production under these experimental conditions.

On the other hand, the addition of inorganic salts has been proposed as another alternative to maximize HMF production [7, 15]. In particular, CaCl_2 has demonstrated to be efficient to accelerate the formation of HMF from glucose as feedstock, due to calcium cations modify the anomeric equilibrium of glucose, favoring the formation of the α anomer more prone to be dehydrated [47, 71, 72]. In this previous work, the effect of chloride anions was also discarded after evaluating that other salts such as NaCl and $(\text{CH}_3)_4\text{NCl}$ did not improve the catalytic performance [51]. Hence, the effect of calcium chloride addition on the catalytic performance of Nb-Zr catalysts was evaluated in this work. From Figure 6A, the influence of calcium cations can be inferred, although it was not similar for all the catalysts. It should be noted that the increase in both glucose conversion and HMF yield values was almost insignificant for the catalysts with the high Nb content, and mainly for Nb_2O_5 . This catalyst was barely affected by the presence of calcium cations. Indeed, a slightly higher glucose conversion (95%) was achieved after 120 min at 175 °C, but HMF yield was maximum after 60 min (41%) and started to decrease after longer reaction times. However, the higher Zr content, the greater influence of CaCl_2 on the catalytic performance. In this sense, Nb_3Zr_7 and ZrO_2 catalysts, which showed a lower catalytic activity in the absence of this salt, now exhibited similar behavior than the rest of materials, in such a way that the presence of CaCl_2 in the reaction medium considerably improved their catalytic performance. Thus, all the catalysts reached almost total conversion of glucose after 120 min, in spite of Nb_2O_5 showed the highest total amount of acid sites, included the presence of Brønsted acid sites. Regarding HMF production, all catalysts were able to provide HMF yields between 40 and 44%, after 60-90 min of reaction, by adding CaCl_2 . It is worth noting that Nb_3Zr_7 and ZrO_2 gave rise to HMF yields close to 45% after 90 min at 175 °C,

whereas these catalysts only attained 20 and 11%, respectively, in the absence of this salt. Therefore, the presence of CaCl_2 did not affect the catalytic performance of these catalysts in the same way. Although it was previously demonstrated by ^1H NMR spectroscopy that Ca^{2+} ions favored the α -D-glucopyranose formation, thus enhancing glucose conversion and HMF yield [47], it would be possible that there was an interaction between these cations and Zr species for Nb_xZr_y and ZrO_2 catalysts, improving their catalytic behavior. This fact could be related to Zr species provided strong Lewis acid sites, not being detected any Brønsted acid sites for these materials. Likewise, catalytic performance achieved after 30 min at 175 °C in the presence of CaCl_2 was also represented as a function of total amount of acid sites (Figure 6B). A linear relationship between catalytic activity and the concentration of acid sites was not found under these experimental conditions, unlike data obtained in the absence of salt. This fact corroborated that the use of CaCl_2 did not affect catalytic performance in the same manner for all the catalysts.

These catalysts were also tested for glucose dehydration into HMF at a lower reaction temperature, 150 °C, always obtaining better catalytic results than the non-catalytic process (without catalyst), both in the absence and in the presence of CaCl_2 (Figure 7). Firstly, the catalytic tests were carried out in the absence of CaCl_2 , attaining the same trend observed at 175 °C. Hence, Nb_2O_5 provided the highest values of glucose conversion and HMF yield in these reaction conditions, 61 and 20%, respectively. However, after addition of CaCl_2 , the HMF yield was hardly improved (23%), although the glucose conversion was increased up to 75%. As previously demonstrated, calcium cations interact with glucose molecules, and it is likely that these cations were able to accelerate the transformation of glucose, increasing conversion; however, these cations

could not promote the HMF production in the presence of Nb₂O₅. After Zr incorporation to niobium oxide, both glucose conversion and HMF yield were lower in the absence of this salt, obtaining the lowest values, 30 and 2%, respectively, for ZrO₂. However, the catalytic activity was improved in the presence of calcium chloride for Nb_xZr_y and ZrO₂ catalysts.

It was demonstrated that all the catalysts possess Lewis acid sites. However, Nb₂O₅ also showed Brönsted acidity, which was not detected for Zr-containing catalysts, only slightly for Nb₇Zr₃. Considering that Lewis acid sites could catalyze the isomerization of glucose to fructose and Brönsted acid sites could promote its subsequent dehydration into HMF, as largely accepted in the literature, a suitable balance between Brönsted and Lewis acid sites could be favorable for the dehydration of glucose to HMF via fructose isomerization [73]. Therefore, Nb₂O₅, which exhibited the presence of both types of acid sites and the highest total concentration of acid sites, was able to provide the greatest values of glucose conversion and HMF yield, also demonstrating that there is a direct relationship between the amount of acid sites and catalytic performance, as was shown in Figure 6A. The decrease in Brönsted acidity and, consequently, in the total acidity after Zr incorporation, could explain the lower activity of Zr-containing mixed oxides. However, the catalytic performance of these latter totally changed by adding CaCl₂, being similar to that found for Nb₂O₅ in the absence of this salt, specially for high Zr contents. Thus, it could be affirmed that the use of calcium chloride was essentially beneficial for Nb_xZr_y and ZrO₂ catalysts, but the catalytic behavior of Nb₂O₅ stayed almost unaltered. In order to check if an interaction between CaCl₂ and zirconium sites could be possible, all catalysts were put in contact with a solution having the same concentration of CaCl₂ (0.65 g_{CaCl2} g_{aq sol.}⁻¹). After this,

catalysts were recovered by filtration and analyzed by HR ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry). The results (Table 2) showed that Ca^{2+} interacted with the catalysts, but the highest concentration of calcium was found in catalysts with high Nb concentration, mainly Nb_2O_5 . This fact could be due to the ionic exchange of protons for calcium cations in Brønsted acid sites. On the other hand, the Zr-containing catalysts displayed the lowest concentrations of calcium, discarding that an interaction between calcium and zirconium was responsible for this improvement of catalytic performance for Zr-containing catalysts. This fact could mean that reaction mechanisms acting in the presence of Nb_2O_5 and ZrO_2 phases were different. Thus, it should be highlighted that all catalysts showed the presence of fructose when dehydration of glucose was carried out in the absence of salt (Figure 5A). Thus, a route in two steps, isomerization of glucose to fructose and its subsequent dehydration to HMF, was probably followed, at least partially, for all tested catalysts (Scheme 1). However, in the presence of CaCl_2 (Figure 6A), fructose was only observed for Nb_2O_5 . García-Sancho et al. previously pointed out that glucose dehydration into HMF in presence of Ca^{2+} could take place following another route rather than classic pathway based on two steps: the isomerization to fructose and subsequent dehydration into HMF [47]. These results were found by using a commercial $\gamma\text{-Al}_2\text{O}_3$ as solid acid catalyst and CaCl_2 , in such a way that fructose concentration was insignificant, not detected by ^1H NMR after heating of D-glucose in presence of this salt. They also affirmed that calcium cations promoted the formation of $\alpha\text{-D-glucopyranose}$ by the formation of complexes with two oxygen atoms. It has been previously proposed an alternative pathway for the direct dehydration of glucose, although is considerably slower than the dehydration via isomerization to fructose, and has been generally associated to the existence of strong

Brönsted acid sites [73-76]. Indeed, Li et al., based on DFT calculations, affirmed that both pathways could contribute to HMF production [77]. On the other hand, Jadhav et al. proposed a mechanism for HMF production via 3-deoxyglucosone, which should be more relevant as intermediate than fructose according to their calculations [[78]. However, they affirmed that its detection was complicated due to its fast transformation, unlike fructose. These authors reported that this mechanism began by elimination of the O3H group of glucose. Considering that calcium cations promoted the formation of α -D-glucopyranose by weak complexes with oxygen atoms, it would be possible that these cations were interacting with O1H and O2H. This fact could facilitate the direct glucose transformation proposed by Jadhav et al. Considering that strong Brönsted acid sites were not found for Nb_xZr_y and ZrO_2 catalysts and the presence of Ca^{2+} improved their catalytic performance without fructose formation, a direct pathway could be followed for dehydration of glucose by using Lewis acid catalysts and CaCl_2 . This fact would also agree with those observed by García-Sancho et al. who barely detected fructose by using alumina, a typical Lewis acid solid, and CaCl_2 [47]. In this sense, calcium cations would promote the formation of α anomer glucose, which should be directly converted to HMF on strong Lewis acid sites of Nb_xZr_y and ZrO_2 catalysts. However, fructose, as reaction intermediate, was detected by using Nb_2O_5 as catalyst in the presence of CaCl_2 , where both Brönsted and Lewis acid sites could promote dehydration via isomerization, even in the presence of this salt. This result agrees with that recently found by Qiu et al. [79], who studied niobium-loaded montmorillonite catalysts for the HMF production, elucidating the mechanism by density functional theory (DFT) calculations. They concluded that these catalysts, which possessed both Brönsted and Lewis acidity, promoted the glucose conversion with relatively low

activation energy via fructose. However, a direct glucose dehydration cannot completely discarded in the presence of Nb_2O_5 and CaCl_2 due to this material also possesses Lewis acid sites.

Finally, a reutilization study was performed with Nb_2O_5 , Nb_5Zr_5 and ZrO_2 catalysts, at 175 °C after 60 min, in the presence of CaCl_2 (Figure 8). After reaction, the catalyst remained inside the reactor, without any type of treatment, and a new mixture (glucose, CaCl_2 and solvents) was added to carry out the reaction under identical experimental conditions. These catalysts maintained their catalytic performance at least for three cycles without any pretreatment after each run. Thus, Nb_2O_5 , Nb_5Zr_5 and ZrO_2 catalysts maintained glucose conversion values of 93-98%, 88-97% and 87-98%, respectively. Moreover, a slight increase in HMF yield was even detected along cycles, specially for Nb_5Zr_5 and ZrO_2 catalysts. This fact was previously observed by Mérida-Morales et al. [71] for mesoporous Zr-doped silica catalysts, demonstrating that this increase was due to the desorption of HMF molecules adsorbed on the catalyst during the first catalytic cycle. Adsorption effects were also reported by Kruger et al. [80]. Therefore, it can be affirmed that both niobium and zirconium oxides are active for dehydration of glucose into HMF and can be reutilized at least for three catalytic runs.

4. Conclusions

Several mesoporous mixed Nb-Zr oxides, including both pure metal oxides, were synthesized by a neutral templating route, and tested for HMF production from glucose. A linear relationship was found between the total amount of acid sites and niobium content, in such a way that pure Nb_2O_5 showed the greatest concentration of

acid sites, as inferred from NH_3 -TPD, as well as a higher surface area and lower crystallinity. This fact led to pure Nb_2O_5 provided the greatest glucose conversion and HMF yield in the absence of salt, due to its higher concentration of acid sites mostly associated to niobium species. Therefore, the total amount of acid sites was a key factor for obtaining higher HMF yields and faster glucose conversion. Moreover, it was observed that catalysts which possessed both Lewis and Brönsted acid sites provided better results (90% conversion and 36% HMF yield for Nb_2O_5) compared to catalysts with poor or none Brönsted acidity (42% conversion and 14% HMF yield for ZrO_2). However, the addition of CaCl_2 to the reaction medium was beneficial for Nb_xZr_y and ZrO_2 catalysts, but the catalytic behavior of Nb_2O_5 remained unaltered, probably due to synergistic effect of calcium ions with Lewis acid sites. Traditionally, it is largely accepted that dehydration of glucose into HMF takes place via fructose isomerization. Although fructose was detected in the reaction media in the presence of catalysts without salt, its absence after the addition of CaCl_2 and Zr-containing catalysts could suggest that glucose may be directly dehydrated to HMF on Lewis acid sites without the formation of fructose as intermediate. Finally, mixed Nb and Zr oxides can be reused at least during three catalytic runs without any pretreatment, maintaining their catalytic performance.

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References

- [1] S. Teong, G. Yi, Y. Zhang, Hydroxymethylfurfural production from bioresources: past, present and future, *Green Chem.*, 16 (2014) 2015-2026.
- [2] P. Zhou, Z. Zhang, One-pot catalytic conversion of carbohydrates into furfural and 5-hydroxymethylfurfural, *Catal. Sci. Technol.*, 6 (2016) 3694-3712.
- [3] J. Bozell, G. Petersen, Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited, *Green Chem.*, 12 (2010) 539-554.
- [4] Z. Xue, M. Ma, Z. Li, T. Mu, Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts, *RSC Adv.*, 6 (2016) 98874-98892.
- [5] D. Zhao, T. Su, Y. Wang, R. Varma, C. Len, Recent advances in catalytic oxidation of 5-hydroxymethylfurfural, *Mol. Catal.*, 495 (2020) 111133.
- [6] N. do Prado, T. Souza, A. Machado, P. Souza, R. Monteiro, L. Oliveira, Enhanced catalytic activity for fructose conversion on nanostructured niobium oxide after hydrothermal treatment: Effect of morphology and porous structure, *J. Mol. Catal. A-Chem.*, 422 (2016) 23-34.
- [7] Y. Roman-Leshkov, J. Dumesic, Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts, *Top. Catal.*, 52 (2009) 297-303.
- [8] X. Tong, Y. Li, Efficient and Selective Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Bronsted-Acidic Ionic Liquids, *ChemSusChem*, 3 (2010) 350-355.
- [9] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenites, *Appl. Catal. A-Gen.*, 145 (1996) 211-224.
- [10] T. Wang, M. Nolte, B. Shanks, Catalytic dehydration of C-6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical, *Green Chem.*, 16 (2014) 548-572.

- [11] R. van Putten, J. van der Waal, E. de Jong, C. Rasrendra, H. Heeres, J. de Vries, Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources, *Chem. Rev.*, 113 (2013) 1499-1597.
- [12] J. Martinez, D. Silva, E. Aguilera, H. Rojas, M. Brijaldo, F. Passos, G. Romanelli, Dehydration of Glucose to 5-Hydroxymethylfurfural Using LaOCl/Nb₂O₅ Catalysts in Hot Compressed Water Conditions, *Catal. Lett.*, 147 (2017) 1765-1774.
- [13] C. Yue, G. Li, E. Pidko, J. Wiesfeld, M. Rigutto, E. Hensen, Dehydration of Glucose to 5-Hydroxymethylfurfural Using Nb-doped Tungstite, *ChemSusChem*, 9 (2016) 2421-2429.
- [14] F. Delbecq, C. Len, Recent Advances in the Microwave-Assisted Production of Hydroxymethylfurfural by Hydrolysis of Cellulose Derivatives-A Review, *Molecules*, 23 (2018) 1973.
- [15] M. Moreno-Recio, J. Santamaría-González, P. Maireles-Torres, Brønsted and Lewis acid ZSM-5 zeolites for the catalytic dehydration of glucose into 5-hydroxymethylfurfural, *Chem. Eng. J.*, 303 (2016) 22-30.
- [16] W. Mamo, Y. Chebude, C. Marquez-Alvarez, I. Diaz, E. Sastre, Comparison of glucose conversion to 5-HMF using different modified mordenites in ionic liquid and biphasic media, *Catal. Sci. Technol.*, 6 (2016) 2766-2774.
- [17] T.D. Swift, H. Nguyen, Z. Erdman, J.S. Kruger, V. Nikolakis, D.G. Vlachos, Tandem Lewis acid/Brønsted acid-catalyzed conversion of carbohydrates to 5-hydroxymethylfurfural using zeolite beta, *J. Catal.*, 333 (2016) 149-161.
- [18] A. Chareonlimkun, V. Champreda, A. Shotipruk, N. Laosiripojana, Catalytic conversion of sugarcane bagasse, rice husk and corncob in the presence of TiO₂, ZrO₂ and mixed-oxide TiO₂-ZrO₂ under hot compressed water (HCW) condition, *Bioresource Technol.*, 101 (2010) 4179-4186.
- [19] V. Ordonsky, J. van der Schaaf, J. Schouten, T. Nijhuis, Glucose Dehydration to 5-Hydroxymethylfurfural in a Biphasic System over Solid Acid Foams, *ChemSusChem*, 6 (2013) 1697-1707.
- [20] M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, Catalytic glucose and fructose conversions with TiO₂ and ZrO₂ in water at 473 K: Relationship between reactivity and acid-base property determined by TPD measurement, *Appl. Catal. A-Gen.*, 295 (2005) 150-156.
- [21] X. Qi, M. Watanabe, T. Aida, R. Smith, Synergistic conversion of glucose into 5-hydroxymethylfurfural in ionic liquid-water mixtures, *Bioresource Technol.*, 109 (2012) 224-228.
- [22] V. Ordonsky, V. Sushkevich, J. Schouten, J. van der Schaaf, T. Nijhuis, Glucose dehydration to 5-hydroxymethylfurfural over phosphate catalysts, *J. Catal.*, 300 (2013) 37-46.

- [23] M. Catrinck, E. Ribeiro, R. Monteiro, R. Ribas, M. Barbosa, R. Teofilo, Direct conversion of glucose to 5-hydroxymethylfurfural using a mixture of niobic acid and niobium phosphate as a solid acid catalyst, *Fuel*, 210 (2017) 67-74.
- [24] R. Weingarten, Y. Kim, G. Tompsett, A. Fernandez, K. Han, E. Hagaman, W. Conner, J. Dumesic, G. Huber, Conversion of glucose into levulinic acid with solid metal(IV) phosphate catalysts, *J. Catal.*, 304 (2013) 123-134.
- [25] J. Zhang, S. Wu, H. Zhang, B. Li, CONVERSION OF GLUCOSE OVER SO₄²⁻/ZRO(2)-TIO₂ CATALYSTS IN AN EXTREMELY LOW ACID SYSTEM, *Bioresources*, 7 (2012) 3984-3998.
- [26] Y. Yang, X. Xiang, D. Tong, C. Hu, M. Abu-Omar, One-pot synthesis of 5-hydroxymethylfurfural directly from starch over SO₄²⁻/ZrO₂-Al₂O₃ solid catalyst, *Bioresource Technol.*, 116 (2012) 302-306.
- [27] E. Ngee, Y. Gao, X. Chen, T. Lee, Z. Hu, D. Zhao, N. Yan, Sulfated Mesoporous Niobium Oxide Catalyzed 5-Hydroxymethylfurfural Formation from Sugars, *Ind. Eng. Chem. Res.*, 53 (2014) 14225-14233.
- [28] I. Nowak, M. Ziolk, Niobium compounds: Preparation, characterization, and application in heterogeneous catalysis, *Chem. Rev.*, 99 (1999) 3603-3624.
- [29] C. Garcia-Sancho, I. Agirrezabal-Telleria, M. Guemez, P. Maireles-Torres, Dehydration of D-xylose to furfural using different supported niobia catalysts, *Appl. Catal. B-Environ.*, 152 (2014) 1-10.
- [30] B. Guo, L. Ye, G. Tang, L. Zhang, B. Yue, S. Tsang, H. He, Effect of Bronsted/Lewis Acid Ratio on Conversion of Sugars to 5-Hydroxymethylfurfural over Mesoporous Nb and Nb-W Oxides, *Chin. J. Chem.*, 35 (2017) 1529-1539.
- [31] C. Garcia-Sancho, J. Rubio-Caballero, J. Merida-Robles, R. Moreno-Tost, J. Santamaria-Gonzalez, P. Maireles-Torres, Mesoporous Nb₂O₅ as solid acid catalyst for dehydration of D-xylose into furfural, *Catal. Today*, 234 (2014) 119-124.
- [32] H. Kreissl, K. Nakagawa, Y. Peng, Y. Koito, J. Zheng, S. Tsang, Niobium oxides: Correlation of acidity with structure and catalytic performance in sucrose conversion to 5-hydroxymethylfurfural, *J. Catal.*, 338 (2016) 329-339.
- [33] F. Yang, Q. Liu, X. Bai, Y. Du, Conversion of biomass into 5-hydroxymethylfurfural using solid acid catalyst, *Bioresource Technol.*, 102 (2011) 3424-3429.
- [34] H. Xiong, T. Wang, B. Shanks, A. Datye, Tuning the Location of Niobia/Carbon Composites in a Biphasic Reaction: Dehydration of D-Glucose to 5-Hydroxymethylfurfural, *Catal. Lett.*, 143 (2013) 509-516.

- [35] X. Li, K. Peng, Q. Xia, X. Liu, Y. Wang, Efficient conversion of cellulose into 5-hydroxymethylfurfural over niobia/carbon composites, *Chem. Eng. J.*, 332 (2018) 528-536.
- [36] F. Huang, T. Jiang, H. Dai, X. Xu, S. Jiang, L. Chen, Z. Fei, P. Dyson, Transformation of Glucose to 5-Hydroxymethylfurfural Over Regenerated Cellulose Supported Nb₂O₅ center dot nH(2)O in Aqueous Solution, *Catalysis Letters*, (2020).
- [37] J. Guo, S. Zhu, Y. Cen, Z. Qin, J. Wang, W. Fan, Ordered mesoporous Nb-W oxides for the conversion of glucose to fructose, mannose and 5-hydroxymethylfurfural, *Appl. Catal. B-Environ.*, 200 (2017) 611-619.
- [38] N. Gromov, O. Taran, V. Semeykina, I. Danilova, A. Pestunov, E. Parkhomchuk, V. Parmon, Solid Acidic NbO_x/ZrO₂ Catalysts for Transformation of Cellulose to Glucose and 5-Hydroxymethylfurfural in Pure Hot Water, *Catal. Lett.*, 147 (2017) 1485-1495.
- [39] I. Jimenez-Morales, J. Santamaria-Gonzalez, A. Jimenez-Lopez, P. Maireles-Torres, Glucose dehydration to 5-hydroxymethylfurfural on zirconium containing mesoporous MCM-41 silica catalysts, *Fuel*, 118 (2014) 265-271.
- [40] W. Zhang, Y. Zhu, H. Xu, M. Gaborieau, J. Huang, Y. Jiang, Glucose conversion to 5-hydroxymethylfurfural on zirconia: Tuning surface sites by calcination temperatures, *Catalysis Today*, (2018).
- [41] D. Stosic, S. Bennici, V. Pavlovic, V. Rakic, A. Auroux, Tuning the acidity of niobia: Characterization and catalytic activity of Nb₂O₅-MeO₂ (Me = Ti, Zr, Ce) mesoporous mixed oxides, *Mater. Chem. Phys.*, 146 (2014) 337-345.
- [42] M. Zakrzewska, E. Bogel-Lukasik, R. Bogel-Lukasik, Ionic Liquid-Mediated Formation of 5-Hydroxymethylfurfural-A Promising Biomass-Derived Building Block, *Chem. Rev.*, 111 (2011) 397-417.
- [43] A. Ranoux, K. Djanashvili, I. Arends, U. Hanefeld, 5-Hydroxymethylfurfural Synthesis from Hexoses Is Autocatalytic, *ACS Catal.*, 3 (2013) 760-763.
- [44] G. Marcotullio, W. De Jong, Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions, *Green Chem.*, 12 (2010) 1739-1746.
- [45] C. Rasrendra, I. Makertihartha, S. Adisasmito, H. Heeres, Green Chemicals from d-glucose: Systematic Studies on Catalytic Effects of Inorganic Salts on the Chemo-Selectivity and Yield in Aqueous Solutions, *Top. Catal.*, 53 (2010) 1241-1247.
- [46] E. Combs, B. Cinlar, Y. Pagan-Torres, J. Dumesic, B. Shanks, Influence of alkali and alkaline earth metal salts on glucose conversion to 5-hydroxymethylfurfural in an aqueous system, *Catal. Commun.*, 30 (2013) 1-4.
- [47] C. Garcia-Sancho, I. Funez-Nunez, R. Moreno-Tost, J. Santamaria-Gonzalez, E. Perez-Inestrosa, J. Fierro, P. Maireles-Torres, Beneficial effects of calcium chloride on

glucose dehydration to 5-hydroxymethylfurfural in the presence of alumina as catalyst, *Appl. Catal. B-Environ.*, 206 (2017) 617-625.

[48] C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi, K. Domen, Highly Active Mesoporous Nb-W Oxide Solid-Acid Catalyst, *Angew. Chem. Int. Ed.*, 49 (2010) 1128-1132.

[49] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, Surface area and pore texture of catalysts, *Catal. Today*, 41 (1998) 207-219.

[50] M. Thommes, K. Kaneko, A. Neimark, J. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.*, 87 (2015) 1051-1069.

[51] M. Yashima, K. Ohtake, M. Kakihana, H. Arashi, M. Yoshimura, Determination of tetragonal-cubic phase boundary of $Zr_{1-x}R_xO_{2-x/2}$ (R = Nd, Sm, Y, Er and Yb) BY Raman scattering, *J. Phys. Chem. Solids*, 57 (1996) 17-24.

[52] J. Jehng, I. Wachs, E. Ko, THE MOLECULAR-STRUCTURES AND REACTIVITY OF SUPPORTED NIOBIUM OXIDE CATALYSTS, *Catal. Today*, 8 (1990) 37-55.

[53] K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. Kondo, S. Hayashi, M. Hara, Nb₂O₅ center dot nH₂O as a Heterogeneous Catalyst with Water-Tolerant Lewis Acid Sites, *J. Am. Chem. Soc.*, 133 (2011) 4224-4227.

[54] C. Liu, W. Wang, Y. Xu, Z. Li, B. Wang, X. Ma, Effect of zirconia morphology on sulfur-resistant methanation performance of MoO₃/ZrO₂ catalyst, *Appl. Surf. Sci.*, 441 (2018) 482-490.

[55] X. Dou, G.-C. Wang, M. Zhu, F. Liu, W. Li, D. Mohan, C.U. Pittman, Identification of Fe and Zr oxide phases in an iron-zirconium binary oxide and arsenate complexes adsorbed onto their surfaces, *J. Hazard. Mater.*, 353 (2018) 340-347.

[56] Y. Gao, Y. Zhang, Y. Zhou, C. Zhang, H. Zhang, S. Zhao, J. Fang, M. Huang, X. Sheng, Synthesis of ordered mesoporous La₂O₃-ZrO₂ composites with encapsulated Pt NPs and the effect of La-doping on catalytic activity, *J. Colloid Interf. Sci.*, 503 (2017) 178-185.

[57] W. Liu, F. Zeng, H. Jiang, X. Zhang, W. Li, Composite Fe₂O₃ and ZrO₂/Al₂O₃ photocatalyst: Preparation, characterization, and studies on the photocatalytic activity and chemical stability, *Chem. Eng. J.*, 180 (2012) 9-18.

[58] S. Jones, L. Neal, M. Everett, G. Hoflund, H. Hagelin-Weaver, Characterization of ZrO₂-promoted Cu/ZnO/nano-Al₂O₃ methanol steam reforming catalysts, *Appl. Surf. Sci.*, 256 (2010) 7345-7353.

- [59] A. Ramanathan, M. Villalobos, C. Kwakernaak, S. Telalovic, U. Hanefeld, Zr-TUD-1: A lewis acidic, three-dimensional, mesoporous, zirconium-containing catalyst, *Chem.-Eur. J.*, 14 (2008) 961-972.
- [60] J. Cecilia, A. Arango-Diaz, J. Marrero-Jerez, P. Nunez, E. Moretti, L. Storaro, E. Rodriguez-Castellon, Catalytic Behaviour of CuO-CeO₂ Systems Prepared by Different Synthetic Methodologies in the CO-PROX Reaction under CO₂-H₂O Feed Stream, *Catalysts*, 7 (2017).
- [61] R. Lopez-Asensio, J. Cecilia, C. Jimenez-Gomez, C. Garcia-Sancho, R. Moreno-Tost, P. Maireles-Torres, Selective production of furfuryl alcohol from furfural by catalytic transfer hydrogenation over commercial aluminas, *Appl. Catal. A-Gen.*, 556 (2018) 1-9.
- [62] J. Gallo, C. Bisio, G. Gatti, L. Marchese, H. Pastore, Physicochemical Characterization and Surface Acid Properties of Mesoporous [Al]-SBA-15 Obtained by Direct Synthesis, *Langmuir*, 26 (2010) 5791-5800.
- [63] P. Carniti, A. Gervasini, F. Bossola, V. Dal Santo, Cooperative action of Bronsted and Lewis acid sites of niobium phosphate catalysts for cellobiose conversion in water, *Appl. Catal. B-Environ.*, 193 (2016) 93-102.
- [64] K. Santos, E. Albuquerque, G. Innocenti, L. Borges, C. Sievers, M. Fraga, The Role of Bronsted and Water-Tolerant Lewis Acid Sites in the Cascade Aqueous-Phase Reaction of Triose to Lactic Acid, *ChemCatChem*, 11 (2019) 3054-3063.
- [65] M. Zaki, M. Hasan, F. Al-Sagheer, L. Pasupulety, In situ FTIR spectra of pyridine adsorbed on SiO₂-Al₂O₃, TiO₂, ZrO₂ and CeO₂: general considerations for the identification of acid sites on surfaces of finely divided metal oxides, *Colloid Surface A*, 190 (2001) 261-274.
- [66] H. Atia, U. Armbruster, A. Martin, Influence of alkaline metal on performance of supported silicotungstic acid catalysts in glycerol dehydration towards acrolein, *Appl. Catal. A-Gen.*, 393 (2011) 331-339.
- [67] C. García-Sancho, J.A. Cecilia, A. Moreno-Ruiz, J.M. Mérida-Robles, J. Santamaría-González, R. Moreno-Tost, P. Maireles-Torres, Influence of the niobium supported species on the catalytic dehydration of glycerol to acrolein, *Appl. Catal. B-Environ.*, 179 (2015) 139-149.
- [68] J. Chheda, Y. Roman-Leshkov, J. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides, *Green Chem.*, 9 (2007) 342-350.
- [69] J. Chan, Y. Zhang, Selective Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Tungsten Salts at Low Temperatures, *ChemSusChem*, 2 (2009) 731-734.

- [70] W. Zhang, Y. Zhu, H. Xu, M. Gaborieau, J. Huang, Y. Jiang, Glucose conversion to 5-hydroxymethylfurfural on zirconia: Tuning surface sites by calcination temperatures, *Catal. Today*, (2018).
- [71] S. Mérida-Morales, C. García-Sancho, M. Oregui-Bengoechea, M.J. Ginés-Molina, J.A. Cecilia, P.L. Arias, R. Moreno-Tost, P. Maireles-Torres, Influence of morphology of zirconium-doped mesoporous silicas on 5-hydroxymethylfurfural production from mono-, di- and polysaccharides, *Catal. Today*, (2020).
- [72] M. Gines-Molina, N. Ahmad, S. Merida-Morales, C. Garcia-Sancho, S. Mintova, N. Eng-Poh, P. Maireles-Torres, Selective Conversion of Glucose to 5-Hydroxymethylfurfural by Using L-Type Zeolites with Different Morphologies, *Catalysts*, 9 (2019).
- [73] P. Zhao, H. Cui, Y. Zhang, Y. Zhang, Y. Wang, Y. Zhang, Y. Xie, W. Yi, Synergetic Effect of Bronsted/Lewis Acid Sites and Water on the Catalytic Dehydration of Glucose to 5-Hydroxymethylfurfural by Heteropolyacid-Based Ionic Hybrids, *Chemistryopen*, 7 (2018) 824-832.
- [74] A. Pedersen, R. Ringborg, T. Grotkjaer, S. Pedersen, J. Woodley, Synthesis of 5-hydroxymethylfurfural (HMF) by acid catalyzed dehydration of glucose-fructose mixtures, *Chem. Eng. J.*, 273 (2015) 455-464.
- [75] Y. Pagan-Torres, T. Wang, J. Gallo, B. Shanks, J. Dumesic, Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Bronsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent, *ACS Catal.*, 2 (2012) 930-934.
- [76] L. Yang, G. Tsilomelekis, S. Caratzoulas, D. Vlachos, Mechanism of Bronsted Acid-Catalyzed Glucose Dehydration, *ChemSusChem*, 8 (2015) 1334-1341.
- [77] J. Li, J. Li, D. Zhang, C. Liu, Theoretical Elucidation of Glucose Dehydration to 5-Hydroxymethylfurfural Catalyzed by a SO₃H-Functionalized Ionic Liquid, *J. Phys. Chem. B*, 119 (2015) 13398-13406.
- [78] H. Jadhav, C. Pedersen, T. Solling, M. Bols, 3-Deoxy-glucosone is an Intermediate in the Formation of Furfurals from D-Glucose, *ChemSusChem*, 4 (2011) 1049-1051.
- [79] G. Qiu, C. Huang, X. Sun, B. Chen, Highly active niobium-loaded montmorillonite catalysts for the production of 5-hydroxymethylfurfural from glucose, *Green Chem.*, 21 (2019) 3930-3939.
- [80] J. Kruger, V. Choudhary, V. Nikolakis, D. Vlachos, Elucidating the Roles of Zeolite H-BEA in Aqueous-Phase Fructose Dehydration and HMF Rehydration, *ACS Catal.*, 3 (2013) 1279-1291.