Niobium Oxides: Correlation of Acidity with Structure and Catalytic Performance in Sucrose Conversion to 5-Hydroxymethylfurfural

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Abstract: The conversion of sugars to 5-hydroxymethylfurfural (HMF) over solid acids in water, represents an environmentally and separation-friendly route to an important platform molecule. In particular, the conversion of sucrose attracts increasing attention because it is cheaper and more widely available than glucose and fructose. Sucrose can undergo rapid hydrolysis to the two monosaccharides, however conversion mechanisms and interactions with solid acids remain unclear. Here, it is shown that niobium oxides possess Brønsted acid (BA) and Lewis acid (LA) sites of tunable quantity and strength, dependent on their structure and morphology. By systematically studying these acid catalysts, it is revealed for the first time that both acid type and strength are significant for the sugars conversion: Fructose reaction is catalyzed by BA, with weaker BA sites being more selective towards HMF. Glucose conversion to HMF involves an additional isomerization step to fructose, which can be catalyzed by both LA and strong BA but LA is more efficient. Sucrose is shown to be easily hydrolyzed into glucose and fructose under the reaction conditions and HMF is formed from the further conversion of the two sugars. It is demonstrated that mesoporous niobium oxide gives the highest HMF yield for sucrose conversion amongst all niobium oxides due to balanced BA and LA sites with appropriate acid strengths.

1. INTRODUCTION

Fossil fuels are currently the main source of both energy and platform molecules for the chemical industry. Rapidly decreasing reserves and growing economic demands raise the need for alternative sources. Biomass is a desirable choice as there is no net carbon emission upon its use. Extensive research over past years has led to the establishment of possible routes to convert biomass to fuels and process chemicals.^{1–4} 5-hydroxymethylfurfural (HMF), derived from sugar molecules, is one of the most promising platform molecules. Various acid catalysts, both homogeneous and heterogeneous, have been employed to convert sugar molecules to HMF. Including the use of different solvents, reaction conditions and types of sugar, large amounts of data have been accumulated.^{5–10} Disregarding the type of catalysts used, it has been found that HMF yield differs significantly with the type of sugar molecule involved. Fructose is generally found to be more reactive and selective towards HMF than glucose. Although these two sugar molecules are isomers to each other and the same number of water molecules are lost during the HMF formation,^{6,11} it is not yet clear why there is a significant difference in their intrinsic reaction rate. Two main reaction pathways for their HMF conversions have been proposed in literature.^{5,6} The acyclic pathway proceeds via open chain intermediates such as 1,2-enediol and 3-deoxyglucos-2-ene common to both glucose and fructose.^{12,13} The cyclic pathway on the other hand, proceeds via closed ring intermediates to HMF from fructose. Glucose conversion involves an extra isomerization step to fructose prior the HMF (Scheme 1).^{14–19} It has been claimed that catalysts with Lewis (LA) and/or Brønsted acid (BA) sites

are needed for both sugars conversions, however there is no agreement amongst researchers which type and strength of acid are required. The mechanisms remain unclear regarding the two forms of sugars and their relationship.^{20,21} In practice, sucrose, a dimer composed of glucose and fructose, is of main industrial interest because it is cheaper and more widely available than its components.²² Although homogeneous acid catalysts, such as organic acids and ionic liquids, can give good yields and selectivities for sugar conversion, extensive product separation procedures make heterogeneous catalysts more attractive. Similarly, separation difficulties are encountered with many yield-enhancing organic solvents employed to extract HMF from aqueous phase. Besides, the use of water as solvent is environmentally friendlier.^{5,7,8} In order to make sucrose conversion scalable and sustainable we may need to consider its catalytic and process features in an industrial and environmental context. This requires an in depth understanding of the underlying reaction mechanisms. However, the conversion of sucrose to HMF in comparison to glucose and fructose has not been investigated in depth yet. Our approach to this challenge is to carry out a systematic study of the conversion of glucose, fructose and sucrose to HMF in water over a variety of structurally related solid niobium oxides. Mechanistically, the conversion of sucrose is closely linked to that of its components glucose and fructose, making it worthwhile to study all three sugars comparatively. Niobium oxides are solid acids consisting of interconnected NbO₆ octahedra with varying extents of structural distortions and defects. Both BA and LA sites have been identified on niobium oxides, with acidic strength dependent on structure

Scheme 1. Dehydration Pathways of Glucose and Fructose: Acyclic Pathway proposed by Anet et al.¹³ and Cyclic Pathway proposed by Assary et al.¹⁷

and environment but the detailed relationship between structure and acidity is not clear.^{23–27} In general, BA sites on metal oxides are associated with strongly acidic hydroxyl groups acting as proton donors and LA sites with exposed oxygen-deficient cations acting as electron pair acceptors.^{28–31} Due to their strongly acidic character, niobium oxides have been studied previously for the sugar conversion, for example, de Souza et al. obtained 28% HMF from glucose in water over NbOH and Carlini et al. achieved 29% HMF from fructose in water over phosphoric acid treated NbOH.^{10,20} However, the catalytic mechanisms have not been studied in detail in the above works, which could help to rationalize the reaction yields.

We are therefore interested in developing niobium oxide as a solid catalyst for the conversion of sucrose to HMF based on a deeper understanding of reaction mechanisms and catalytic features. Using TMP (trimethylphosphine) ³¹P NMR we have been able to measure the acid properties of different niobium oxides more accurately than previous measurement techniques such as CO, pyridine FTIR and NH₃ TPD.³² The detailed information obtained, in combination with structural analysis by Raman, TEM and XRD, enables us to gain new insights into how acidity correlates with structure in this compound group. Further, catalytic conversions over the niobium oxides for glucose, fructose and sucrose to HMF have been compared systematically. This offers some unique mechanistic insights into the sugars conversion, by correlating acid type and strength to fundamental reaction steps. We are able to demonstrate that mesoporous niobium oxide amongst all the different types of niobium oxide catalysts studied, gives the highest HMF yield from sucrose due to the balanced BA and LA sites of its structure with appropriate acidic strengths. Overall, we believe this study offers some new essential

information, which will lead to a more rational design of solid acid catalysts for the sugars conversion.

2. EXPERIMENTAL

A variety of niobium oxides, ranging from bulk to multi- to monolayer structures has been synthesized according to reported methods. So far no comparative study of these compounds has been conducted, neither regarding structural aspects nor acid catalytic properties. The bulk material HNb₃O₈ has been prepared by a conventional solid-state reaction of the precursors K₂CO₃ and Nb₂O₅, followed by proton exchange. Few layer niobium oxide (hy-Nb) and monolayer niobium oxide (hy-Nb-TEOA) have been synthesized from Nb(OEt)₅ in ammonia solution, in the case of hy-Nb-TEOA under further addition of triethanolamine (TEOA). Both materials have been acid treated before use, in order to remove the basic surfactant species blocking their acid sites. Mesoporous Nb₂O₅ has been prepared by hydrolysis and condensation of Nb(OEt)₅, followed by soaking in acid solution. Detailed synthetic procedures are given in the Supporting Information (SI). For comparison, commercial bulk Nb₂O₅ (Alfa Aesar) was also used. In terms of characterization, our focus is to correlate acidity with structure, since a variety of niobium oxides of different structures are used as acid catalysts for the conversion of sugars to HMF. The acid sites were thus first characterized using conventional Hammett indicators. Since niobium oxides are generally associated with strong acidity, their pK_a values are outside the normal pH range, requiring the use of the Hammett function.^{28,33,34} Therefore, a series of indicators was used to determine the acid strength (pK_a), followed by titration with n-butylamine for quantification.^{26,28,35} Another study, employing trimethylphosphine (TMP) adsorption followed by ³¹P MAS NMR (TMP NMR) measurements, was conducted. The acid type, LA or BA, and acid strength can be clearly differentiated by the ³¹P chemical shift of TMP due to

Table 1. Surface Area and Acid Site Analysis of Niobium Oxide Catalysts

Catalyst	SA (m ² g ⁻¹)	Type and amount (μmol g ⁻¹) by TMP ³¹ P	TMP ³¹ P NMR shift of acid sites (ppm)	Acid strength pK _a by Hammett indicator	Amount of acid sites (μmol g ⁻¹) by Hammett titrations
Nb ₂ O ₅	3	ND	ND	ND	ND
HNb ₃ O ₈	10	BA (30) no LA	BA: - 2.77	-5.6 < pK _a < -3.0	50 ^a ; 100 ^b
hy-Nb-TEOA	121	BA (171) LA (108)	BA: - 0.36 LA: - 24.98	-5.6 < pK _a < -3.0	300 ^a ; 200 ^b
hy-Nb	166	BA(259) LA(269)	BA: - 0.87 LA: - 42.27	-5.6 < pK _a < -3.0	800 ^a ; 600 ^b
Meso-Nb ₂ O ₅	142	BA(338) LA(222)	BA: - 5.47 LA: - 25.37	-5.6 < pK _a < -3.0	600 ^a ; 550 ^b

SA (Surface Area; error ± 1 m² g⁻¹); BA (Brønsted acid); LA (Lewis acid); ND (not detected)

^a values obtained using dicinnamalacetone indicator in benzene;

^b values obtained using methyl red indicator in water.

the variations in interaction strength of the adsorbed TMP molecule with different acid sites. (0 to -6 ppm is typically associated with BA; -20 to -45 ppm with LA; the less negative the shift value, the stronger the acidity). Furthermore, quantitative analysis of the ^{31}P NMR peaks was carried out.^{36,37} For more information on Hammett indicator and TMP ^{31}P MAS NMR measurements, see SI. In order to gain further structural insights, TEM, surface area measurements, Raman spectroscopy and XRD were also acquired. TEM images of the samples were recorded using a JEM-2100F instrument (JEOL Ltd.). Specific surface areas were derived from corresponding adsorption isotherms with a conventional BET nitrogen adsorption apparatus (BELSORP18SP, Bell Japan Inc.), see SI. Raman spectra were collected on a Perkin Elmer Raman Spectrum 400F. Powder XRD was conducted using monochromatized Cu K α radiation at 40 kV and 40 mA on a Rint2500X, Rigaku Corp.

Reactions over the niobium oxide catalysts were performed inside an autoclave at 500 rpm stirring speed and at 180°C. 1wt% sugar in water and 1wt% catalyst, were used to give a total reaction mixture volume of 15 mL. Aqueous samples were taken from the autoclave with a dip tube at regular intervals ranging from 1 to 180 minutes. During sampling, the reaction was quenched by immersing the autoclave into an ice bath and the reaction was resumed by re-heating it to 180°C. The formation of HMF and the sugar consumption were monitored over time by analysis of each sample collected using high performance liquid chromatography (HPLC).

Figure 1. Catalysts Surface Areas

Figure 2. Catalysts Acid Site Quantities

Figure 3. Schematic Drawing of TMP Adsorption on Acid Sites

Figure 4. TEM Images of Catalysts

Figure 5. Acid Site Quantity (Peak Area) and Strength (Chemical Shift: the less negative the higher the acid strength) of Catalysts from TMP ^{31}P NMR

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalyst Acidity and Structure

Different forms of niobium oxide give different surface areas, as shown by BET of nitrogen adsorption measurements (Figure 1). Similarly large variations are found regarding acidity. By comparing the TMP NMR acidity (Figure 2) and Hammett indicator measurements over the different forms of niobium oxide (Table 1), it can be seen that TMP NMR gives more detailed information. By means of ^{31}P chemical shift values, BA and LA are easy to differentiate and variations in acid strength of both sites can be displayed (Table 1, Figure 3). Hammett indicators are useful to visualize the range of acid strengths of the niobium oxides, but they failed to deliver precise values because of the limited number of commercially available indicators within the required pK $_a$ range. Further, a differentiation between BA and LA is unfortunately not possible with the Hammett indicators.^{26,28,35} In terms of acid site quantification, TMP NMR is also more accurate since titration with Hammett indicators poses problems such as color change/end point determination, mass transfer limitations and catalyst dispersion, etc. Despite the fact that the TMP NMR and Hammett indicator measurements did not yield the same values, the trends in acid quantities are the same: the amount of total acid sites increases

in the order of $\text{Nb}_2\text{O}_5 \ll \text{HfNb}_3\text{O}_8 < \text{hy-Nb-TEOA} < \text{hy-Nb} < \text{mesoporous Nb}_2\text{O}_5$, which is closely related to their surface areas. From TEM (Figure 4) commercial Nb_2O_5 (4a) clearly appears as a bulk material with extremely low surface area, accounting for the reason why the quantities of acid sites are well below the detection limits for both TMP NMR and Hammett measurements. Although HfNb_3O_8 (4b) is also in bulk form, it shows more irregularities on particle edges and a sheet-like structure, resulting in a higher surface area. For hy-Nb-TEOA (4c) and hy-Nb (4d), much smaller and thinner nano-sheet like fragments are observed leading to considerably higher surface areas. For hy-Nb and hy-Nb-TEOA, previous work has shown that their structures resemble that of HfNb_3O_8 , but in few-layer form for hy-Nb and monolayer form for hy-Nb-TEOA. Particularly, TEOA as a surfactant can restrict structural grow along the c-axis, which results in monolayer formation.³⁸ It is interesting to observe a higher surface area and higher acid quantity (Figure 5) of the hy-Nb compared to hy-Nb-TEOA, presumably due to a higher degree of layer re-stacking with higher porosity of the latter. Mesoporous Nb_2O_5 (4e) in contrast appears to be more worm-like with many pores and holes, suggesting its highly amorphous nature.

According to XRD patterns (Figure 6a and SI) HfNb_3O_8 (after calcination) is a highly crystalline material consisting of alternating layers of negatively charged NbO_6 octahedra and protons.^{33,34,39} The hy-Nb and hy-Nb-TEOA materials show similar diffraction patterns to that of HfNb_3O_8 however the peaks are much broader (Figure 6b and SI). This indicates that they share the basic structural features of HfNb_3O_8 , but their layer thickness and structural order have been greatly reduced (SI). Raman spectroscopy (Figure 7) clearly supports these findings. As the crystallinity progressively decreases from HfNb_3O_8 to hy-Nb and then to hy-Nb-TEOA, the observed peaks become broader. According to literature, the Raman region at higher wavenumbers of 850-1000 cm^{-1} represents distorted octahedra (double-bond like Nb-O) in the NbO_6 structure.^{23,40} By comparing the peak size in this region, one could arrange the degree of octahedral distortion as hy-Nb-TEOA > hy-Nb >> HfNb_3O_8 . Interestingly, their measured Lewis acid strength (Table 1 and SI) follows the same order. This suggests that Lewis acidity is correlated to the degree of structural distortion. Because of its very broad spectrum and amorphous structure, no clear peak can be seen in the region of 850-1000 cm^{-1} for the mesoporous Nb_2O_5 . The high Lewis

Figure 6. XRD patterns of a) HfNb_3O_8 b) hy-Nb and hy-Nb-TEOA

Figure 7. Raman spectra of niobium oxide catalysts

Figure 8. Proposed structure of a) mesoporous Nb_2O_5 , b) monolayer hy-Nb-TEOA c) few-layer hy-Nb and d) bulk HfNb_3O_8 with terminal and bridging hydroxyl groups

acidity associated with this amorphous material (LA: - 25.37) could not thus be directly verified, but is thought to relate to its structural disorder.

In the BA region, we have found broad peaks with peak maxima ranging from -0.36 to -5.47 ppm (Figure 5 and Table 1) for the niobium oxides. Peak deconvolution of the TMP NMR spectra reveals at least two types of acid (see SI). The first deconvoluted peak at 0 to -1.5 ppm can be assigned to a strong BA site and the second peak at -4 to -6 ppm to a weaker BA site. Crystalline HNb_3O_8 , hy-Nb and hy-Nb-TEOA materials all contain both BA types, but mesoporous Nb_2O_5 seems to only possess the weaker BA site. It is to note that the strongly acidic BA site on Group IV-VI oxides is associated with bridging hydroxyl groups between octahedra with shared edges or faces while the weaker BA corresponds to a proton localized on a terminal oxygen.^{29,32} As a result, the analysis of BA by TMP NMR spectroscopy can reflect the degree of connectivity of NbO_6 octahedra over the different forms of niobium oxides. Clearly, the amorphous nature of mesoporous Nb_2O_5 is structurally different from crystalline HNb_3O_8 , hy-Nb and hy-Nb-TEOA. Due to its low structural order, it appears to possess disordered corner shared octahedra with only terminal hydroxyls, hence giving exclusively the weaker BA sites (Figure 8a). On the other hand, the layered structure of HNb_3O_8 contains stacked NbO_6 octahedra with shared edges or faces giving hydroxyls of stronger acidity, besides its terminal hydroxyls of weaker acidic nature (Figure 8d). The same applies to hy-Nb (Figure 8c) and hy-Nb-TEOA (Figure 8b), which are similar to HNb_3O_8 in structure but with reduced layer thickness, as discussed earlier. The increase in quantity and strength of BA of hy-Nb and hy-Nb-TEOA compared to HNb_3O_8 can be assigned to their decrease in layer-thickness and increase in structural distortion, resulting in more acidic bridging hydroxyls.

3.2. General Observations Regarding Sugar Conversion

It is noted that the reaction pathways for sugars conversion are complicated and hence it may be difficult to select a simple parameter to indicate catalytic performance. Although HMF is our main target product it is kinetically unstable to other oxygenated or condensed side products. There are co-existences of different types and quantities of acid sites with different strengths on our niobium oxide samples that will lead to different rates of HMF production and some can catalyze further conversion of HMF to side products. Thus, it may be difficult to use rates of reaction for comparison (for example, stronger BA gives a higher rate of fructose conversion but the selectivity for HMF is lower). For a batch process, the maximum yield of HMF obtained before further degradation over a solid catalyst is the key experimental parameter. Thus, the maximum yield is used for comparison. On the other hand, initial reaction rates can be informative in parallel with the yield comparison, thus they are also included and discussed in the Table 2 and SI. As seen, fructose is converted faster than glucose under the same reaction conditions as evidence from its higher rates of reaction compared to glucose over all catalysts tested (Table 2). Fructose also tends to give higher HMF yields than glucose at

optimal time (Figure 9). These observations are consistent with previous reports in literature.^{11–18,20} However it is interesting to note that although the general trend is for fructose to give higher yields, some of the catalysts we tested reach the same HMF yield for both glucose and fructose. This suggests that glucose can be converted to HMF as efficiently as fructose, if appropriate acid sites are used. Regarding sucrose conversion, it is found in this work that HMF yields are intermediate of these of glucose and fructose (Figure 9 and 10a). Further, analysis shows that after the first measurement, there is no sucrose left in the reaction mixture. Instead, its components glucose and fructose are detected instantly at large amounts, which progressively decrease with time in a comparable manner to the conversion of pure glucose and fructose (Figure 10b and SI). This indicates that sucrose is readily hydrolyzed into its two components glucose and fructose at high temperatures and that HMF is then formed from them individually and independently. This observation also explains why the HMF yields from sucrose are always intermediate of that of glucose and fructose (Figure 9 and 10a). For reaction profiles of all catalysts, see SI. When comparing the initial reaction rates in Table 2, glucose and fructose as components of sucrose give only slightly lower rates than pure glucose and fructose, which can be explained by the short additional off-set time it takes to hydrolyze sucrose into its components before their further conversion.

3.3. Influence of Acid Strength on Sugar Conversion

Studying sugar conversion over the various niobium oxides, the following order for HMF yield from glucose is observed: mesoporous Nb_2O_5 (36%) > hy-Nb (32%) > hy-Nb-TEOA (28%) > HNb_3O_8 (18%) > Nb_2O_5 (13%) > no catalyst (5%). Interestingly, the order for HMF yield from fructose is found to be different from that of glucose, with mesoporous Nb_2O_5 (36%) > HNb_3O_8 (34%) > hy-Nb (30%) > hy-Nb-TEOA (27%) = Nb_2O_5 (27%) = no catalyst (27%) (Table 2, Figure 9).

Also, for fructose, this order does not correlate with acid site quantities or surface areas (Figure 1 and 2). Larger amounts of acid sites do have a positive effect on the rate of reaction with faster conversion for higher acid quantities (compare Table 2 and Figure 2), as would be expected. In terms of HMF yield though, acid quantity variations within the range of the tested niobium oxide catalysts do not show an effect. This is likely caused by acid quantities large enough to reduce all activity to the catalyst surface with no competitive in-solution processes. Instead, variations in acid type and strength of the catalytic sites are found to be key factors in determining the sugar conversion selectivity towards HMF, in form of HMF yield versus side products obtained. An inverse correlation between HMF yield and BA strength is noted for fructose: the lower the BA site strength, the higher the HMF yield. For example, hy-Nb-TEOA, with -0.36 ppm TMP ^{31}P NMR chemical shift showing the strongest BA, gives only 27% HMF (the same as without catalyst) < hy-Nb (-0.87 ppm) with 30% HMF < HNb_3O_8 (-2.77 ppm) with 34% HMF < mesoporous Nb_2O_5 (-5.47 ppm) with 36% HMF. (For simplicity, the position of BA peak maxima of TMP NMR was directly compared using the original spectra without quantitative deconvolution, Table 1 and Figure 5).

Table 2. Experimental Results of Sugar Conversion over the Catalysts in Water

Catalyst	Sugar	HMF yield (%)	Relative Rates of Sugar Conversion ^a
None	Glucose	5	1
	Fructose	27	3
	Sucrose	13	1 (Glucose component) ^b 2 (Fructose component) ^b
Nb ₂ O ₅	Glucose	13	8
	Fructose	27	16
	Sucrose	17	6 (Glucose) ^b 12 (Fructose) ^b
HNb ₃ O ₈	Glucose	18	14
	Fructose	34	26
	Sucrose	25	12 (Glucose) ^b 24 (Fructose) ^b
hy-Nb-TEOA	Glucose	28	30
	Fructose	27	34
	Sucrose	27	24 (Glucose) ^b 30 (Fructose) ^b
hy-Nb	Glucose	32	32
	Fructose	30	40
	Sucrose	32	30 (Glucose) ^b 34 (Fructose) ^b
meso Nb ₂ O ₅	Glucose	36	36
	Fructose	36	40
	Sucrose	36	32 (Glucose) ^b 36 (Fructose) ^b

Reactions were performed at 180°C using 1wt% sugar in water and 1wt% catalyst.

^a Initial reaction rates are estimated based on the conversion (%) of the sugar after the first 5min in the batch reactor at steady temperature and are expressed as a relative value to that of glucose substrate without catalyst

^b no sucrose is left even at the first measurement after 1min, therefore the conversion rates of the hydrolysed components, glucose and fructose, are expressed (see reaction profiles in Figure 10 and SI)

No apparent correlation can be found for LA strength and even further, the presence itself of LA sites does not seem to affect fructose conversion, for example similar HMF yields are obtained from HNb₃O₈ (no LA) and mesoporous Nb₂O₅ (with 222 $\mu\text{mol g}^{-1}$ large LA quantity, Figure 2). Overall, this leads us to conclude that for fructose conversion, the presence of LA sites does not significantly affect HMF yield while the presence of BA sites increases HMF yield, with weaker BA sites being better promoters than stronger BA sites. Stronger BA sites increase the formation of more stable oxygenated products other than HMF during sugar conversion, such as alcohols and organic acids (HPLC analysis). As a control experiment, fructose was converted using HCl (aq), a much weaker BA than those on niobium oxide surfaces, due to the formation of H₃O⁺.⁴¹ We indeed obtained much higher HMF yields at a comparably low rate of conversion (63% HMF from 0.01M HCl at a relative sugar conversion rate of 11) with the HCl concentration in the same range as BA site amounts. (Possible chloride ion interference was ruled out in

Figure 9. HMF yield obtained from glucose, fructose and sucrose over the different catalysts

Figure 10. Exemplary Reaction Profile of Sugar Conversion over Time on Nb₂O₅ with a) HMF yields of Glucose, Fructose and Sucrose b) Conversion of Glucose, Fructose and Sucrose

another control experiment by adding sodium chloride to the sugar solution, which gave the same result as that of no catalyst/additive.) It is evident that HCl, forming H₃O⁺ and Cl⁻ in water as a much weaker BA ($\text{pK}_a(\text{H}_3\text{O}^+) = -1.74$)⁴¹ than our solid acid catalysts ($-5.6 < \text{pK}_a < -3.0$, Table 1), is significantly more selective in the conversion of fructose to HMF. Similarly, hydrolysis of transition metal chlorides in water can give H₃O⁺ for high conversion of fructose to HMF.¹⁹ The comparably high HMF yield of 27% obtained from fructose in pure water without catalyst (Table 2) can also be explained by the strongly enhancing effect of H₃O⁺: Very small concentrations of H₃O⁺ (10^{-14} mol/l at 25°C) are present due to the natural dissociation of water, which increases with temperature.⁴¹ The amounts of H₃O⁺ present under the reaction conditions are obviously far below the range of the acid quantities of the tested catalysts and

therefore water cannot match the performance of HCl or the weaker BA niobium oxides. Although the H_3O^+ quantities are so low, water promotes fructose conversion to HMF to a yield comparable to that of the strong BA niobium oxide catalysts, only at a slower rate of reaction, which underlines that weaker BA is much more selective towards HMF than strong BA. Looking at the differences in catalytic performance between H_3O^+ , such as formed from HCl in water (63% HMF yield), and BA sites on solid acid catalysts such as HNb_3O_8 (34% HMF yield), it can be concluded that even when using water as the reaction medium the strong BA sites (H^+) on niobium oxides remain mostly intact and do not significantly form weak BA adducts with water (H_3O^+). Literature has also shown this assumption to be valid: Niobium oxides, as opposed to many other solid catalysts, retain their acid site activity in water.^{25,26,29} Nakajima *et al.* have shown BA sites to remain fully and LA sites partially intact for niobium oxides in water.³¹

For glucose conversion, the increase in HMF yield using solid acid catalysts is much more apparent than for fructose. This indicates that more acid catalyzed reaction steps must be involved in glucose conversion than for fructose. The HMF yield increases in the order of no catalyst < Nb_2O_5 < HNb_3O_8 < hy-Nb-TEOA < hy-Nb < mesoporous Nb_2O_5 (Figure 9). As for fructose, a control experiment using 0.01M HCl (aq) was carried out, with no chloride ion effect, and yielding 9% HMF at a relative sugar conversion rate of 2. This is only a very small increase in HMF yield compared to no catalyst, with still mostly side products being formed. When using the much stronger solid BA catalyst HNb_3O_8 , significantly more HMF (18%) can be obtained, indicating that strong BA promotes glucose conversion, while the effects of weaker BA are, if any, marginal. The best performance though is shown by the niobium oxides which possess LA besides BA sides (hy-Nb-TEOA, hy-Nb and mesoporous Nb_2O_5 , Figure 2). For these catalysts, HMF yields from glucose reach the same values as obtained from fructose (Figure 9), demonstrating the superior capability of LA to convert glucose compared to BA. Differences in LA site strength do not seem to play a role, at least not the variations in LA strength present among our catalysts. Overall, it is found that glucose conversion is catalyzed primarily by LA and to a lesser extent by strong BA, with weak BA being insignificant. Interestingly, for all catalysts, HMF yield from glucose can reach up to but does not exceed to that of fructose.

3.4. Mechanistic Elucidations

We have shown that fructose to HMF reaction is catalyzed by BA of niobium oxides, while glucose to HMF conversion is promoted by LA of the solid catalysts. Thus, the catalytic acid properties required for the formation of HMF apparently differ significantly for the two sugars. In contrast, the acyclic

pathways in literature involve the formation of common key intermediates from enol-keto tautomerism for both glucose and fructose (Scheme 1)^{5,12,13}, thus a similar nature of acid sites for catalytic conversion is expected. In fact, both glucose and fructose transitions *via* 1,2-enediol and 3-deoxyglucos-2-ene are thought to be base or LA catalyzed (Lobry de Bruyn-Alberda van Ekenstein transformation).^{14,42-44} However, our study shows that fructose conversion to HMF is in contrary a BA catalyzed step, therefore it does not seem to match with the proposed acyclic pathways. On the other hand, for the proposed cyclic pathways, glucose conversion to HMF involves the isomerization of glucose to fructose as an additional rate-limiting step before the conversion of fructose to HMF (Scheme 1).^{5,14-19} Indeed, we have observed a clear difference in catalytic efficiencies using niobium oxides of different LA and BA quantities and strengths. Also, upon HPLC analysis of the sugar conversion products with time, glucose gives significant amounts of 10-15% fructose as reaction intermediate over all catalysts, while fructose gives <4% glucose intermediate. This shows that isomerization of the two sugars takes place in both directions, but glucose isomerization to fructose is much more significant. This further supports our argument that glucose conversion requires the formation of fructose before further conversion to HMF, while fructose is directly converted to HMF. Experimentally it is also shown that HMF yield from glucose can approach but does not exceed that of fructose, strongly indicating a step-wise conversion with fructose as key intermediate. Overall, our results clearly endorse the cyclic pathway. A stepwise reaction mechanism is summarized in Scheme 2: Glucose to fructose isomerization is catalyzed by strong BA and LA, with LA being much more selective. Weak BA on the other hand is required for the conversion of fructose to HMF. Sucrose, as shown earlier in the sugar reaction profile section (Figure 10 and SI), is easily hydrolyzed into its components glucose and fructose at high temperatures and HMF is formed from the further conversion of these two components. Side reactions play a rather significant role in sugar conversion to HMF in water, with about 40% even when optimising reaction conditions therefore they are also included in the scheme. Regarding the individual steps in sugar conversion to HMF over the niobium oxides, we propose the following catalytic mechanisms: For the glucose to fructose isomerization step, we propose that the catalyzed reaction proceeds primarily on exposed Nb^{5+} in distorted NbO_6 octahedra (LA), while the further conversion of fructose to HMF is promoted mainly by weak terminal acidic hydroxyls (BA), as shown in Scheme 3. As a final note, we have discounted the possibility of niobium oxide dissolution to form other catalytic species under our reaction conditions, with the weights of the solid catalysts remaining unchanged before and after the reactions.

Scheme 2. Catalytic Steps of Sucrose to HMF Conversion

Scheme 3. Proposed Mechanisms for a) Glucose to Fructose Isomerization and b) Fructose to HMF Conversion

a) Glucose to Fructose Isomerization via LA-hydrate intermediate (upper pathway) or LA-1,2-enediol intermediate (lower pathway)

b) Fructose to HMF conversion

4. CONCLUSIONS

In summary, we have used a combined approach of structural and catalytic performance studies to elucidate the mechanistic details of sugar to HMF conversion over niobium oxides.

Using TMP NMR as a tool to analyze surface acidity gives much more detailed information than previous measurement techniques. By further performing TEM, **surface area measurements**, XRD and Raman spectroscopy, we have been able to gain new insights into structure and acidity relationships. LA sites appear to originate from a distorted octahedral NbO_6 structure. The higher the structural distortion as reflected by Raman spectroscopy in the region of $850\text{--}1000\text{ cm}^{-1}$, the stronger the LA sites produced. Further, strongly acidic BA sites can be associated with bridging hydroxyls between edge-shared octahedra, weaker BA on the other hand with terminal hydroxyls. Few- and monolayer niobium oxides give rise to particularly strong BA sites compared to bulk material, possibly due to structural deformation. Further to structural investigations we have tested catalytic activities for glucose, fructose and sucrose conversion to HMF. For the first time we have been able to show that both acid type and strength are closely linked to the catalytic performance: Fructose conversion to HMF is catalyzed by BA, with weaker BA sites being more selective towards HMF. By far the highest HMF yield is obtained using the comparably weak BA H_3O^+ rather than solid acids. Glucose conversion to HMF involves the isomerization of glucose to fructose as an additional step. This isomerization is catalyzed by both LA and strong BA, though LA appears to be much more efficient, with a selectivity of up to 100%. The catalytic effect of a weaker BA such as H_3O^+ seems to be insignificant. Sucrose is shown to be easily hydrolyzed into its components glucose and fructose at high temperatures and HMF is formed from the further conversion of these two components. It is demonstrated that mesoporous niobium oxide gives the overall highest HMF yield for sucrose conversion, due to the balanced BA and LA of its structure with the most appropriate acid strengths for the conversion of both glucose and fructose component.

5. OUTLOOK

Sucrose is shown to be rapidly hydrolyzed into its components, glucose and fructose, under the reaction conditions. Therefore its efficient further conversion to HMF requires a combined catalytic approach, with both LA and weak BA sites present, in order to convert both glucose and fructose to HMF. Thus, mesoporous niobium oxide from the tested catalysts gives the highest HMF yield in sucrose conversion. So far the BA strength of solid acid catalysts, even when using water as the solvent, is much higher than that of H_3O^+ formed by an aqueous inorganic acid such as HCl. It might be worth exploring solid LA catalysts in combination with an aqueous inorganic acid as BA. Unfortunately, we have been unable to fully block the BA sites on our niobium oxide catalysts so far, but further investigations are underway. Overall, sucrose conversion to HMF in water over niobium oxide catalysts is both an environmentally and separation-friendly process. Therefore, rationally designed solid acid catalysts with tunable acidity are certainly a promising approach to sucrose conversion and worth-wile to be investigated further.

ASSOCIATED CONTENT

Supporting Information

Section 1: Material synthesis information including XRD patterns in Figure S1-2 and BET measurements in Figure S3; Section 2: Hammett indicator measurements; Section 3: TMP ^{31}P MAS NMR analysis including background information, sample preparation, measurement procedure, modes of TMP adsorption in Figure S4, TMP measurement set-up in Figure S5, calibration curve in Figure S6, peak deconvolution in Figure S7 & Table S1; Section 4: Reaction profiles for sugar conversion and HMF yield in Figure S8.

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GRAPHICAL ABSTRACT