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Effect of Brønsted/Lewis Acid Ratio on Conversion of Sugars to 5-Hydroxymethylfurfural over Mesoporous Nb and Nb-W Oxides

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A series of mesoporous Nb and Nb-W oxides were employed as highly active solid acid catalysts for the conversion of glucose to 5-hydroxymethylfurfural (HMF). The results of solid state ^{31}P MAS NMR spectroscopy with adsorbed trimethylphosphine as probe molecule show that the addition of W in niobium oxide increases the number of Brønsted acid sites and decreases the number of Lewis acid sites. The catalytic performance for Nb-W oxides varied with the ratio of Brønsted to Lewis acid sites and high glucose conversion was observed over Nb_5W_5 and Nb_7W_3 oxides with high ratios of Brønsted to Lewis acid sites. All Nb-W oxides show a relatively high selectivity of HMF, whereas no HMF forms over sulfuric acid due to its pure Brønsted acidity. The results indicate fast isomerization of glucose to fructose over Lewis acid sites followed by dehydration of fructose to HMF over Brønsted acid sites. Moreover, comparing to the reaction occurred in aqueous media, the 2-butanol/H_2O system enhances the HMF selectivity and stabilizes the activity of the catalysts which gives the highest HMF selectivity of 52% over Nb_7W_3 oxide. The 2-butanol/H_2O catalytic system can also be employed in conversion of sucrose, achieving HMF selectivity of 46% over Nb_5W_5 oxide.

Keywords carbohydrates, glucose, HMF, Nb-W oxide, heterogeneous catalysis

Introduction

Biomass as a renewable feedstock has been intensively studied for the production of fuel and fine chemicals.[1-8] Carbohydrates, the most important fractions of biomass and the largest natural source of carbon, show great potential for the production of useful platform chemicals such as 5-hydroxymethylfufural (HMF).[9-13] As a platform chemical, HMF can be converted to useful products, such as 2,5-furandicarboxylic acid to replace terephthalic acid in the polyethylene terephthalate industry and adipic acid used in the nylon industry.[14-15]

The C_6 sugars, glucose and fructose, have been employed as feedstocks for the formation of HMF. Fructose dehydration to HMF can be realized over Brønsted acid sites more easily than glucose because the reactivity of fructose (ketose) is higher than that of glucose (aldose) in aqueous solution. Great success has been achieved on fructose dehydration to HMF over homogeneous and heterogeneous acidic catalysts in aqueous[16] or multiphase systems[12,17,18] and ionic liquids.[19-23] However, the low price and high availability of glucose in comparison with fructose make it more reasonable to be a better feedstock. Unfortunately, the direct dehydration of glucose leads to low selectivity of HMF due to side reactions like unselective condensation of glucose to by-products such as humins.[24] The yield of HMF can be increased significantly by initial isomerization of glucose to fructose over Lewis acid sites in tandem with dehydration of fructose over Brønsted acid sites.[25] Hence, the challenge to transform glucose to HMF is to develop catalysts and reaction systems which can achieve balanced functions of the isomerization of glucose to fructose and the dehydration of fructose to HMF.

Zhao *et al.* reported the highest HMF yield of near 70% in ionic liquids with $CrCl_2$ catalyst.[26] Since then, many studies have been explored in similar catalytic system of different metallic salts in acidic medium, such as $AlCl_3$ combined with Brønsted acid HCl,[17,24] water-compatible lanthanide-based Lewis acids in biphasic systems,[27] and $Zr(O)Cl_2/CrCl_3$ catalyst in *N*,*N*-dimethyl acetamide solvent containing LiCl under microwave assisted heating.[28] Other studies were also carried out

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in aqueous system with $ZnCl_2$,[29] $CrCl_3$[30] and WCl_3[31] catalysts. However, the main disadvantages of all these catalytic systems are high costs of ionic liquids, corrosion in the use of minerals acids, or difficult recovery of catalysts from the reaction medium. For industrial applications, heterogeneous catalysts are more preferred in the reaction of glucose to HMF.

Niobic acid ($Nb_2O_5{\bullet}nH_2O$)[32] and hydrated tantalum oxide ($Ta_2O_5{\bullet}nH_2O$)[33] which have both Brønsted and Lewis acidities display remarkable activity in the dehydration of glucose to HMF. Moreover, mesoporous materials like tantalum oxide,[34,35] zeolite Sn-beta[36] and TiO_2[37] have also been employed as catalysts. In a similar way, surface modified metal oxides such as SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2-Al_2O_3,[38] metal(IV) phosphates[39-40] and phosphate/TiO_2[41] can somehow inhibit side reactions and improve HMF selectivity. However, the possible leaching of sulfate or phosphate species may cause a poor catalyst reusability, as reported for sulfated zirconia, tantalum phosphate and niobium phosphate.[35,42-43] Recently, Guo *et al.*[44] studied the catalytic activity of Nb-W oxides on glucose dehydration to HMF in aqueous system at 120 ℃. However, systematic investigations, especially the addition of organic phase to achieve high catalytic performance, are still worth being carried out for better understanding the relationship between the Brønsted/Lewis acidity and catalytic activity.

In this work, we studied the role of the type and amount of Lewis and Brønsted acid sites on different mesoporous niobium oxides and Nb-W oxides with specific ratios of Nb to W in the transformation of glucose to HMF. Moreover, the influences of different experimental parameters, such as adding organic phase, reaction temperature and time, dosage of catalyst, along with reusability, have been evaluated to achieve high catalytic performance.

Experimental

Catalyst preparation

Mesoporous niobium oxide with amorphous walls was prepared following the procedures previously reported by our laboratory under controlled relative humidity using triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, Sigma Aldrich), niobium pentachloride ($NbCl_5$, 99＋%, Strem Chemicals) and *n*-propanol.[45] The solution containing 2.56 g of P123, 20 g of *n*-propanol, and 3.78 g (14 mmol) of $NbCl_5$ was stirred vigorously at room temperature for 30 min, then 2 g of de-ionized water was added with further stirring for *ca.* 2 h. The resulting sol was gelled on a glass plate at 40 ℃ under controllable humidity of *ca.* 45% for 5 d. The aged gel sample was calcined at 450 ℃ for 5 h in air to remove the block copolymer surfactant.

Mesoporous Nb-W oxides with different Nb/W molar ratio, Nb_5W_5, Nb_7W_3 and Nb_9W_1, were synthesized by dissolving 2.56 g of P123, 20 g of *n*-propanol, and desired amount of WCl_6 (99＋%, Strem Chemicals) and $NbCl_5$ (total of 12 mmol of metal chloride) with vigorous stirring at room temperature for 30 min, then 1.08 g of de-ionized water was added with further stirring for *ca.* 2 h. The resulting sol was gelled on a glass plate at 40 ℃ under controllable humidity of *ca.* 45% for 5 d. The aged gel samples were calcined at 460 ℃ for 5 h in air to remove the block copolymer surfactant.

$Nb_2O_5{\bullet}nH_2O$ was prepared following a procedure reported by Nakajima *et al.*[32] A mixture of $NbCl_5$ (5 g) and de-ionized water (200 mL) was stirred at room temperature for 3 h. The white precipitate was filtered and then washed several times with de-ionized water until neutral. The sample was finally dried overnight at 353 K.

Catalyst characterization

The textural properties of the catalysts were evaluated from nitrogen adsorption-desorption isotherms at 77 K, using a Quantachrome Quadrasorb SI apparatus. The samples were degassed at 523 K for 3 h before each experiment. The surface areas were calculated using the BET method. Pore size distribution curves were derived from the desorption branches of isotherms and calculated by the BJH model. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM2010 transmission electron microscope. Solid-state nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance III 400 spectrometer. High-power ^1H decoupling ^{31}P magic angle spinning (MAS) NMR spectra were acquired at 161.9 MHz using a 30° pulse and a recycle delay of 15 s at a spinning rate of 12 kHz with 4 mm zirconia rotor. $NH_4H_2PO_4$ was used as a standard sample for chemical shift referencing (δ 0.81) and the external intensity standard to quantify the signal. Trimethylphosphine (TMP) was employed as a probe molecule for the acidity study. About 200 mg of powdered sample was placed in a home-made glass tube and activated at 300 ℃ for 90 min under vacuum (10^{-1} Pa) to ensure maximum adsorption of TMP molecules by using a vacuum system. Then, the sample tube was flame sealed for storage and transferred in a glovebox under nitrogen atmosphere in order to repack the TMP-adsorbed samples into a Bruker 4 mm ZrO_2 rotor.

Catalytic activity measurement

The catalytic reaction was carried out in a 50 mL autoclave and heated in a temperature controlled oil bath with magnetic stirring. The reaction was performed by using 0.1 g of catalyst and 5 mL of 2 wt% of substrate. For the 2-butanol/H_2O catalytic reaction system, 2-butanol was introduced to aid in removing the formed HMF from catalyst surface. In this way, the further degradation of HMF can be suppressed.[12] Typically, a 2-butanol/H_2O (5 ∶ 2, *V*/*V*) system was performed by using 0.05—0.3 g of catalyst and 2 mL of 1 wt%—10 wt% of substrate and 5 mL of 2-butanol. The reactor was raised to certain temperature and held for a given reaction time. After reaction, the reactor was quenched immediately with cold water. In both aqueous and 2-butanol/H_2O systems the mixture was centrifuged and the liquid samples were filtered through a 0.25 μm filter before analysis. Liquid samples were analyzed by HPLC equipped with refractive index and UV-Vis detectors at wavelength of 284 nm with a Biorad© Aminex HPX-87H sugar column. The mobile phase was 0.005 mol/L H_2SO_4 aqueous solution flowing at a rate of 0.6 mL/min at 35 ℃.

Results and Discussion

Physico-chemical properties of the catalysts

Nitrogen adsorption-desorption isotherms and the pore size distribution of the Nb-W oxides are shown in Figure 1. All the samples show the type IV isotherms with a clear hysteresis loop, suggesting the presence of typical mesopores. Table 1 and Figure 1b show that the BET specific surface area decreased from 174 $m^2 \cdot g^{-1}$ to 26 $m^2 \cdot g^{-1}$ with the increase of tungsten content, accompanied with the decrease of pore volume from 0.32 $cm^3 \cdot g^{-1}$ to 0.21 $cm^3 \cdot g^{-1}$ and the pore diameter from 7.4 (mesoporous niobium oxide) to 6.0 nm (mesoporous Nb_5W_5 oxide). TEM images of these Nb-W oxides are shown in Figure 2. It can be seen that all the oxides have wormlike mesopores, and a slight decrease of uniformity was observed for Nb_5W_5 oxide with relatively high amount of tungsten.

A number of techniques may be used in the study of acidity of solid catalysts, such as pyridine-IR, NH_3-TPD and NMR. The main drawback of NH_3-TPD is not able to distinguish between Brønsted acid and Lewis acid, as well as their subtle differences in the distribution, while pyridine-IR is very difficult to study acid density quantitatively. ^{31}P MAS NMR with trimethylphosphine (TMP) as the probe molecule has the advantages of distinguishable and assignable peaks and may provide comprehensive information on the acid type, strength distribution and relevant density.[47-50] Herein, the acid property of Nb-W oxides was evaluated by ^{31}P MAS NMR spectroscopy using TMP as a probe molecule.

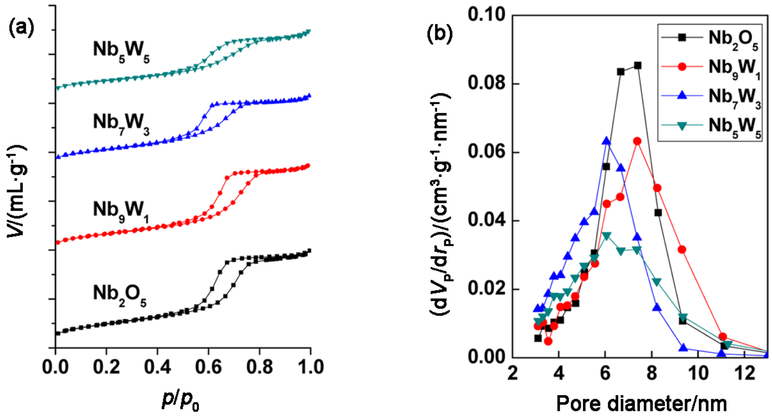


Figure 1 (a) N_2 adsorption-desorption isotherms of Nb-W oxides, (b) pore size distributions of Nb-W oxides.

Table 1 Characterization of the catalysts

Catalyst	$S_{BET}/(m^2 \cdot g^{-1})$	Pore volume/$(cm^3 \cdot g^{-1})$	Pore diameter/nm	Brønsted acid/$(\mu mol \cdot g^{-1})$	Lewis acid/$(\mu mol \cdot g^{-1})$	B/L
Nb_2O_5	174	0.32	7.4	63	203	0.31
Nb_9W_1	152	0.30	7.3	72	116	0.62
Nb_7W_3	146	0.22	6.1	154	84	1.83
Nb_5W_5	126	0.21	6.0	112	89	1.26

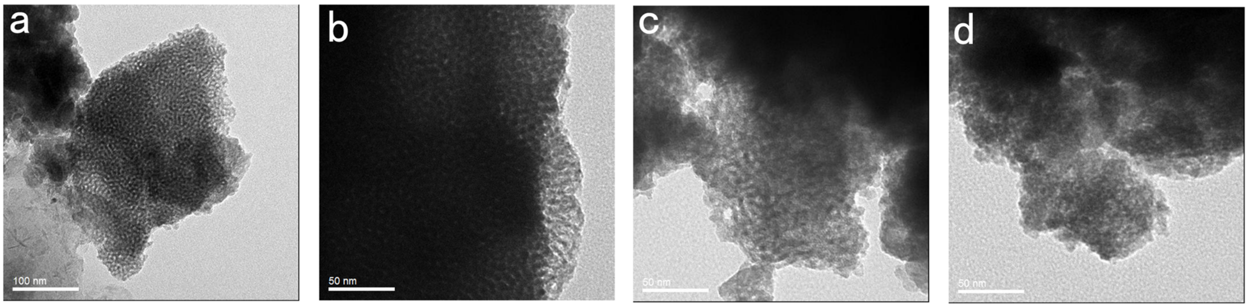
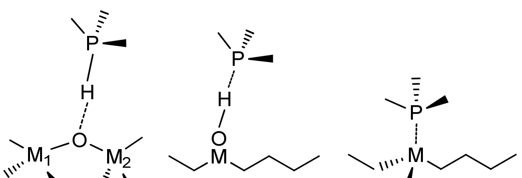


Figure 2 TEM images of (a) Nb_2O_5, (b) Nb_9W_1, (c) Nb_7W_3 and (d) Nb_5W_5 oxides.

There are three different types of adsorbed TMP as shown in Scheme 1. TMP tends to form protonated adducts, giving rise to ^{31}P resonances in a rather narrow range of δ −2 to −5.[51] The chemical shift from δ −20 to −50 is assigned to TMP on Lewis acid sites, which is more sensitive to the strength of Lewis acid than that of Brønsted acid.[46] The ^{31}P MAS NMR spectra of mesoporous niobic oxide and Nb-W oxides are shown in Figure 3. The broad peak at *ca.* δ 62 could be assigned to trimethylphosphine oxide (TMPO) interacting with Brønsted acid sites,[52] which was observed on all mesoporous niobic oxide and Nb-W oxides. The existence of TMPO is possibly due to the oxidation of TMP on the surface of mesoporous niobic oxide and Nb-W oxides. The ^{31}P chemical shifts of TMP on Lewis acid sites tended to shift to high field (from δ −37.4 to −50.6) with increasing tungsten content, indicating the created Lewis acid sites by addition of tungsten in niobium oxide are usually weaker than the Lewis acid sites initially present on the niobium oxides. It suggests that the addition of tungsten in niobium oxide results in partial replacement of Nb^{5+} ions by higher-valence W^{6+} ions, leading to increase of the number of Brønsted acid sites (as shown in Table 1) formed by bridged hydroxyl groups (Nb-(OH)-W). However, the slight decrease of Brønsted acid sites of Nb_5W_5 oxide is mainly caused by decreasing of surface area and possible formation of amorphous surface polytungstate species with high amount of tungsten.[53,54] Lewis acid sites in Nb oxide are mostly generated from NbO_4 tetrahedra and highly distorted NbO_6 octahedra. It can be anticipated that the addition of tungsten in niobium oxide generates more perfect octahedra, with the decreasing of Lewis acid sites from 203 μmol/g of Nb_2O_5 to 89 μmol/g of Nb_5W_5 oxide.

Scheme 1 Three types of adsorbed trimethylphosphine: (a) chemisorbed on Brønsted acid sites, (b) physisorbed on hydroxyls (hydrogen bonding interaction) and (c) chemisorbed on Lewis acid centers[46]



Glucose dehydration in aqueous phase

It is well known that the transformation process of glucose over heterogeneous catalysts is rather complicated due to a number of parallel reactions.[40] As shown in Scheme 2, glucose could be dehydrated to cellobiose and levoglucosan; saccharides could polymerize with reaction products containing aldehyde group such as HMF and furfural, leading to forming water soluble polymers and water insoluble humins;[55,56] subsequently, rehydration of HMF to levulinic acid and formic acid could be favored in aqueous system.[57]

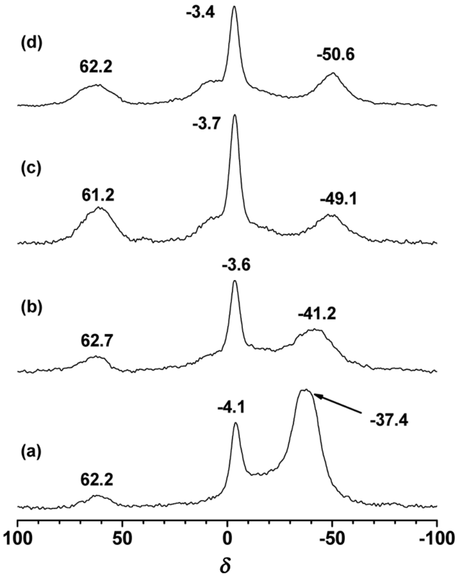
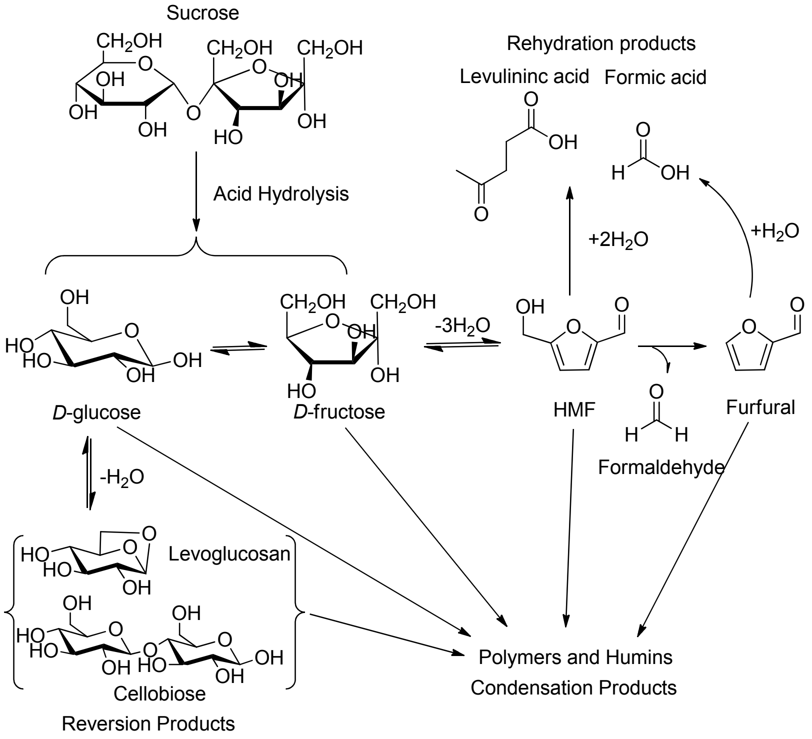


Figure 3 ^{31}P MAS NMR spectra of (a) Nb_2O_5, (b) Nb_9W_1, (c) Nb_7W_3 and (d) Nb_5W_5 adsorbed with TMP.

Figure 4a shows the glucose conversion as function of reaction time for various Nb-W oxide catalysts. All mesoporous Nb and Nb-W oxide catalysts show higher glucose conversion compared to that of sulfuric acid (SA) which has no Lewis acidity. On the other hand, mineral acid SA shows glucose conversion of <10% even after 360 min reaction. Therefore, it clearly indicates that Lewis acidity plays a significant role in glucose conversion. In general, the dehydration of glucose to HMF proceeds through a tandem pathway including isomerization of glucose to fructose over Lewis acid and succeeding dehydration of fructose to HMF over Brønsted acid.[2,25,30,58] Glucose conversion over all three Nb-W oxides with different Nb/W ratios increases in the order of $Nb_7W_3 > Nb_5W_5 > Nb_9W_1$, which is consistent with the trend of the ratios of Brønsted to Lewis acid sites (as shown in Table 1). Higher glucose conversion was observed for Nb_5W_5 and Nb_7W_3 oxides which have relatively high ratios of Brønsted to Lewis acid sites.

As mentioned above, the dehydration of glucose to HMF is a tandem reaction including isomerization of glucose to fructose and fructose dehydration to HMF. Hence, the selectivity of fructose is expected to be relative with the balance of isomerization and dehydration. As shown in Figure 4b, the fructose selectivities over all catalysts are not higher than 4%, which are much lower than those over solid acid catalysts such as mesoporous tantalum oxide,[34] metal(IV) phosphates,[40] sulfated zirconia[42] and combination of Amberlyst-15 and hydrotalcite.[59] The fructose selectivity over Nb_2O_5 decreases from 4% at 60 min to 1% after 360 min of the reaction. At the same time, fructose could hardly be detected over Nb_5W_5 and Nb_7W_3 oxide catalysts. The absence of fructose could be attribute to the fast dehydra-

Scheme 2 Reaction pathway for conversion of saccharides to HMF



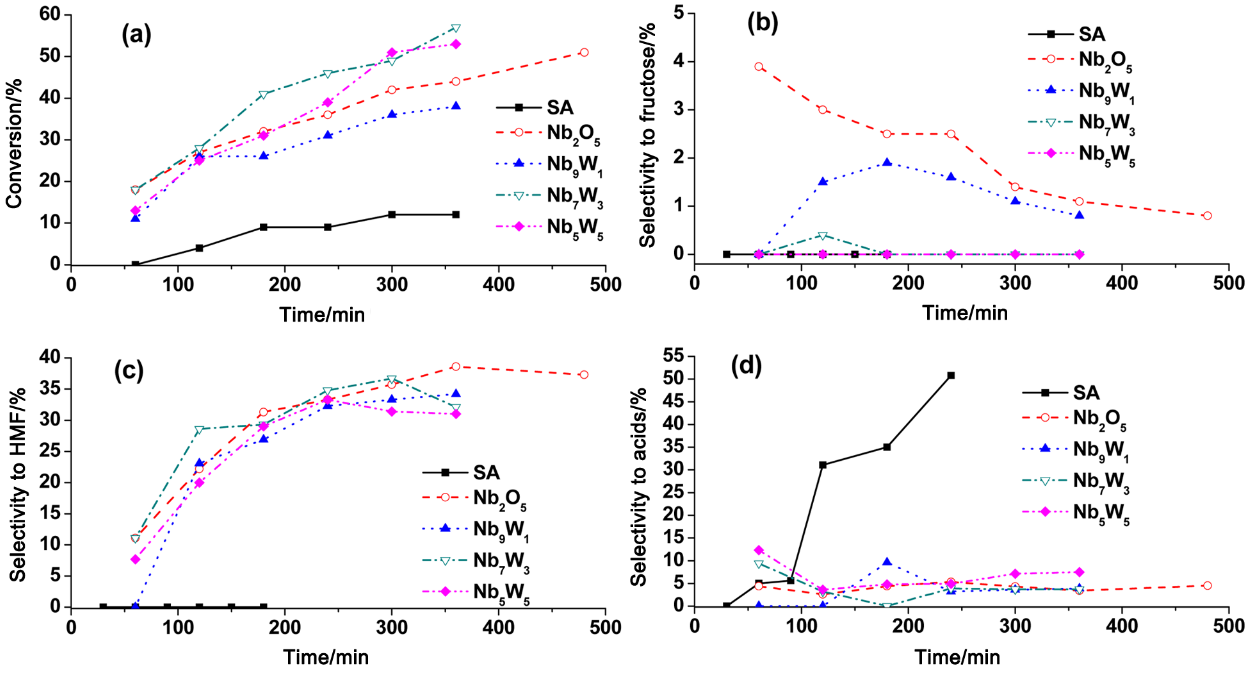


Figure 4 Glucose conversion (a), selectivity to fructose (b), HMF (c) and acids (d) versus reaction time over different catalysts. Reaction conditions: 0.1 g catalyst, 5 mL of 2 wt% *D*-glucose solution were stirred in an autoclave at 140 ℃.

tion of fructose to HMF over catalysts with more Brønsted acid sites. These results could also be explained by another proposed mechanism which is suitable for solid acid catalysts with both Brønsted acid sites and Lewis acid sites, *i.e.* isomerization of glucose over Lewis acid sites accompanied with dehydration to HMF over Brønsted acid sites without intermediate desorption of fructose molecules.[39]

The selectivity to HMF over different catalysts is shown in Figure 4c. A similar trend of HMF selectivity was observed for all catalysts. The HMF selectivity firstly increased then decreased with increasing reaction times, owing to rehydration of HMF to levulinic acid, formic acid over Brønsted acid sites and condensation to soluble polymers and humins over Lewis acid sites.[30,39,40,55] The HMF selectivity reached a maximum value of 33% over Nb_5W_5 oxide after 240 min and 37% over Nb_7W_3 oxide after 300 min. On the other hands, the HMF selectivities over Nb_2O_5 and Nb_9W_1 oxides with relatively high amount of Lewis acid sites achieve their maximum value at longer reaction time than Nb_7W_3 and Nb_5W_5 oxides with high amount of Brønsted acid sites. No HMF was observed for pure SA, possibly due to low yield of HMF and easy hydration of HMF with mineral acid in aqueous catalysis system, which could be confirmed by low conversion of glucose and low selectivity of fructose over SA.

The selectivity to levulinic acid and formic acid is shown in Figure 4d. A relatively higher acids selectivity was observed for SA in comparison with Nb-W oxide catalysts, ascribing to easier rehydration of HMF to levulinic acid and formic acid over SA with only Brønsted acidity. This is in agreement with the results over aluminum phosphate and titanium phosphate catalysts,[39] where high selectivity to acids was found to become more significant when the catalyst has a low activity in the dehydration of the more stable glucose molecule. For SA, the selectivity to acids increased fast to 51% after 240 min reaction time at glucose conversion even below 10%. At the same time, no HMF was observed due to the low conversion of glucose and easy rehydration of HMF over mineral acid in aqueous catalytic system. In contrast, the selectivity to acids over Nb-W oxide catalysts was in the range of 3%—7% even after 360 min reaction time.

On the basis of our results above, it possibly enlightens us on design and preparation of solid acid catalysts for effective conversion of glucose to HMF. Our results demonstrate clearly the importance and necessity of both Brønsted and Lewis acid sites in an effective catalyst. First, the activation of glucose molecule occurs preferentially over Lewis acid sites. Thus, in order to obtain a considerable conversion of glucose, catalysts with Lewis acidity other than pure SA should be chosen. Once glucose isomerization succeeds over Lewis acid sites, formed fructose needs to be dehydrated to HMF by Brønsted acid. However, the existence of side-reactions, such as condensation of sugars and HMF over Lewis acid sites[30,39,40,55] and rehydration of HMF over Brønsted acid sites, demands the suitable ratios of Brønsted to Lewis acid sites which in turn achieves high selectivity to HMF.

It is noteworthy that the mass balance is not satisfied on all Nb-W oxide catalysts after summation of the selectivity of all detected main products like fructose, acids and HMF. Approximately 50%—60% of glucose is transformed into humins, which cannot be detected by HPLC and GC-MS. In general, humins were considered as all unidentified water soluble and insoluble polymers. The formation of humins can be mainly attributed to the aldol condensation of HMF and unreacted saccharides with formyl groups (—CHO) in the presence of acid catalysts.[60,61] Thus, the selectivity of HMF can be theoretically improved by using a biphasic system, where the formed HMF may be dissolved in the organic phase and separated from the aqueous media containing unreacted saccharides for suppression of HMF rehydration and condensation with saccharides.[18]

Glucose dehydration in 2-butanol/H_2O system

As far as we know, various organic solvents have been used in biphasic system for conversion of saccharides to HMF. Among them, solvents with four carbon atoms (C_4) like 2-butanol were commonly used and showed the highest affinity for HMF, coupled with low water miscibility at the reaction temperature.[9,10,12,33] In the present case, we also studied the performances of other organic solvents such as THF, MIBK, DMSO at first. 2-Butanol and MIBK exhibited similar high value of HMF selectivity. However, MIBK has a higher HMIS health hazard rating than 2-butanol,[24] thus 2-butanol was chosen in consideration of enviromental impact and cost-effective chemical principle. Further glucose dehydration studies were carried out with mesoporous Nb_2O_5 in a 2-butanol/H_2O system, where the yields of fructose and acids were extremely low, and therefore, we focused on only production of HMF.

The influence of solvent dosage on the glucose conversion as well as the selectivity to HMF was investigated. Figure 5 shows glucose dehydration over niobium oxide in the presence of different dosage of 2-butanol. Extraction of HMF by 2-butanol, which is visible by a colorless aqueous phase and a brown organic phase, shows a clear water/oil interface in Figure S1a†. Without an addition of 2-butanol, the selectivity to HMF is 35% at nearly 100% glucose conversion. After the addition of 2-butanol (2-butanol/H_2O = 2 : 2, *V*/*V*) the selectivity significantly increases to 41%. The catalytic results reflect that the selectivity of HMF can be improved by adding 2-butanol for distracting the formed HMF from catalyst surface and suppressing further rehydration and condensation of HMF. It is noticeable that the water/oil interface disappears with increasing the 2-butanol/H_2O ratio to 5 : 2 (*V*/*V*) since pure 2-butanol is partially miscible with water.[12] However, at a 2-butanol/H_2O ratio of 5 : 2 (*V*/*V*), the selectivity to HMF keeps at about 42%. This high HMF selectivity is possibly due to improving activity of the catalyst by removing humins deposed on the surface of the catalyst with organic solvent. However, the addition of excessive 2-butanol (2-butanol/H_2O = 7 : 2, *V*/*V*) may lead to desorption of fructose from active sites which accounts for the decreasing HMF selectivity.

The influence of the reaction temperature has been investigated at a 5 : 2 *V*/*V* ratio of 2-butanol/H_2O. As shown in Figure 6, at low temperature of 80 ℃ and 100 ℃, only 5% and 17% of HMF selectivity can be obtained, respectively. As the apparent activation energy associated with the HMF formation from fructose is higher compared with that of glucose isomerization,[30]

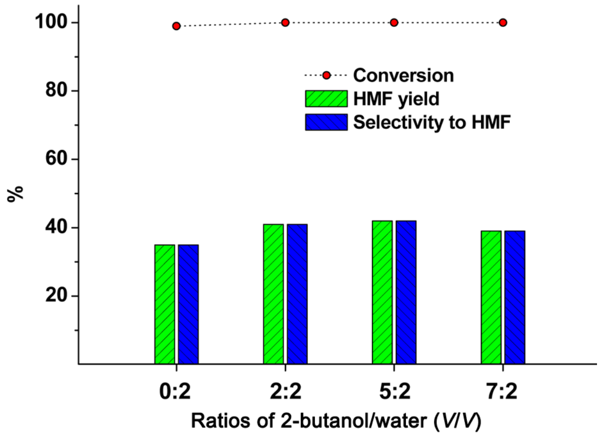


Figure 5 Comparison of different ratios of 2-butanol/H_2O for the conversion of glucose into HMF over Nb_2O_5. 0.2 g of catalyst, 2 mL of 1 wt% *D*-glucose and desired volume of 2-butanol were stirred in an autoclave at 140 ℃ for 2 h.

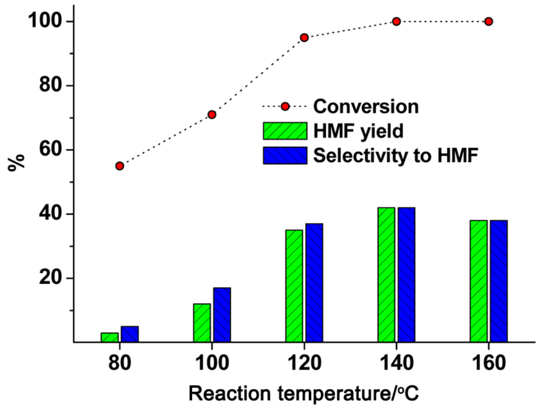


Figure 6 Comparison of different reaction temperature for the conversion of glucose into HMF over Nb_2O_5. 0.2 g of catalyst, 2 mL of 1 wt% *D*-glucose and 5 mL of 2-butanol (2-butanol/H_2O=5∶2, *V*/*V*) were stirred in an autoclave at set temperature for 2 h.

only 3% of HMF yield was achieved at 80 ℃ with more than 55% of glucose conversion. In addition, only a small amount of fructose can be detected, which is very common in the published studies of glucose dehydration to HMF over an effective solid acid catalyst.[32,34,37-39,41] Since there are many parallel reactions in the transformation process of glucose over solid acid catalysts, the formation of a number of reversion and epimerization intermediates such as mannose and enediol could increase the glucose transformation.[25,40,41,61] With increasing reaction temperature to 120 ℃, the HMF yield increases up to 35% with 95% of glucose conversion and the selectivity of HMF increases slowly above 120 ℃. The catalytic results reflect that glucose conversion and HMF selectivity increase with increasing reaction temperature, achieving the highest values at 140 ℃. At higher reaction temperature, the side reactions such as HMF rehydration and condensation result in the decrease of HMF selectivity. Thus, 140 ℃ was selected as the optimized reaction temperature to study other parameters influencing the catalytic reaction.

Figure 7 shows the catalytic performance with different reaction time. The reaction is extremely fast, as 75% of glucose conversion was achieved after 30 min. In the 2-butanol/H_2O system, the addition of 2-butanol leads to a fast transformation of glucose to HMF due to the equilibrium shifts towards the HMF formation by partitioning of HMF from sugar reactants. Similar observations were obtained in previous studies where solid metal phosphate catalysts with relatively high Brønsted to Lewis ratios were used.[33-35,37,40] These results demonstrate that the first step of glucose isomerization is very fast, and formed intermediates may occupy some active sites initially which could slow down subsequent reaction. The selectivity to HMF increases with the reaction time, attaining the maximum value of 42% after 2 h. However, further prolonging reaction time causes slight decrease of HMF selectivity, possibly due to the preferential rehydration of HMF in aqueous media or condensation of HMF (Figure S1c†). Thus, 2 h was selected as the optimal reaction time.

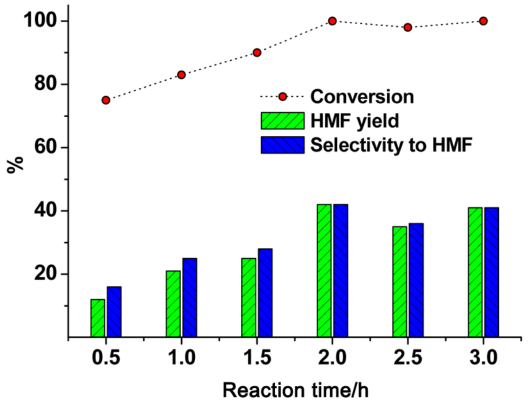


Figure 7 Comparison of different reaction time for the conversion of glucose into HMF over Nb_2O_5. 0.2 g of catalyst, 2 ml of 1 wt% *D*-glucose and 5 mL of 2-butanol (2-butanol/H_2O=5∶2, *V*/*V*) were stirred in an autoclave at 140 ℃.

Figure 8 shows the catalytic performance with different catalyst dosage for the conversion of glucose into HMF. With only 0.05 g of Nb_2O_5, 90% of glucose conversion and 27% of HMF selectivity are obtained. However, without addition of Nb_2O_5, glucose conversion is only 15%. With increasing dosages of catalyst to more than 0.1 g, almost 100% conversion of glucose is obtained. Regarding the selectivity of HMF, it monotonously increases with increasing the dosages of catalyst and achieves the maximum value (42%) with 0.2 g of catalyst. However, beyond 0.2 g of catalyst the selectivity of HMF can hardly be improved and remains approximately 40%.

The glucose conversion and HMF selectivity decrease when the initial glucose concentration increases from 1 wt% to 10 wt% (Figure 9). The change of HMF selectivity is in agreement with literature reports that increasing the initial saccharide concentration leads to

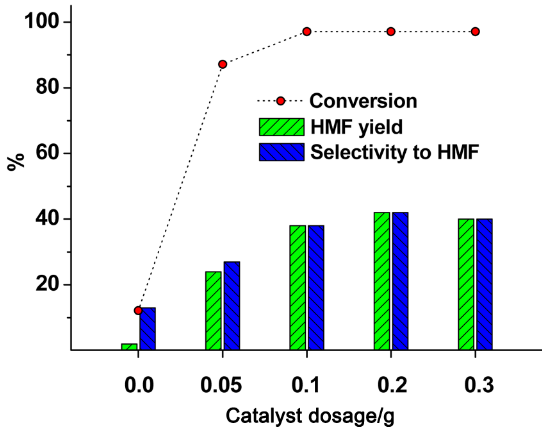


Figure 8 Comparison of different catalyst dosage for the conversion of glucose into HMF. Nb_2O_5 was used as catalyst, 2 mL of 1 wt% *D*-glucose and 5 mL of 2-butanol (2-butanol/H_2O=5∶2, *V*/*V*) were stirred in an autoclave at 140 ℃ for 2 h.

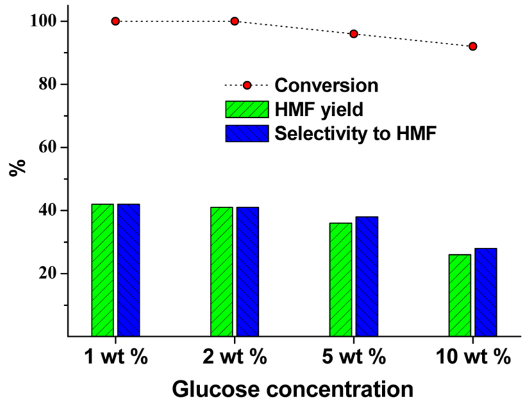


Figure 9 Comparison of different glucose concentration for the conversion of glucose into HMF over Nb_2O_5. 0.2 g of catalyst, 2 mL of 1 wt% *D*-glucose and 5 mL of 2-butanol (2-butanol/H_2O= 5∶2, *V*/*V*) were stirred in an autoclave at 140 ℃.

high probability of side reactions between fructose and HMF.[61,62] However, it should be noted that the decrease of HMF selectivity is larger than that of glucose conversion. Although high catalytic activity (92% conversion of glucose) is maintained with 10 wt% of initial glucose concentration, excessive unreacted glucose and formed HMF exist, leading to side reactions such as condensation and rehydration which are favored in aqueous media. In Figure S1e† one may see the color of reaction liquids changes from light brown to dark with increasing the initial glucose concentration from 1 wt% to 10 wt%, in agreement with the formation of more soluble polymers and humins at higher initial glucose concentration. Thus, it can be deduced from Figure 9 that, catalytic system with low initial glucose concentration could be used to minimize side reactions of HMF and sugars. For this reason, high glucose concentrations may not be advisable in a one-pot catalytic system.

With the optimized reaction conditions in the 2-butanol/H_2O system, the reusability of Nb_2O_5 and Nb_7W_3 oxide catalysts was evaluated. Figure 10 depicts the results of six consecutive runs over both catalysts. Between each run, the catalyst was simply recovered by washing with 10 mL of deionized water three times before drying at 120 ℃ for 2 h. In the consecutive experiments no significant decreases in conversion and selectivity were observed. The reusability of the present catalysts is better than the reported results where the apparent loss of catalytic activity was observed due to the blockage of acid sites by formed humins.[35,38,42,43] Moreover, in the conversion of glucose with the similar Nb-W oxide catalyst in aqueous system at 120 ℃, Guo *et al.* still found noticeable decrease of catalytic performance even after re-calcination of Nb_4W_4 under 400 ℃ for 4 h to remove residue.[44] This clearly reveals that the 2-butanol/H_2O system enhances the HMF selectivity and stabilizes the activity of the catalysts. Therefore, it can be concluded that the Nb and Nb-W oxide catalysts are effective catalysts for the conversion of glucose to HMF in a 2-butanol/H_2O system. Among them, Nb-W oxide catalyst shows better catalytic performance.

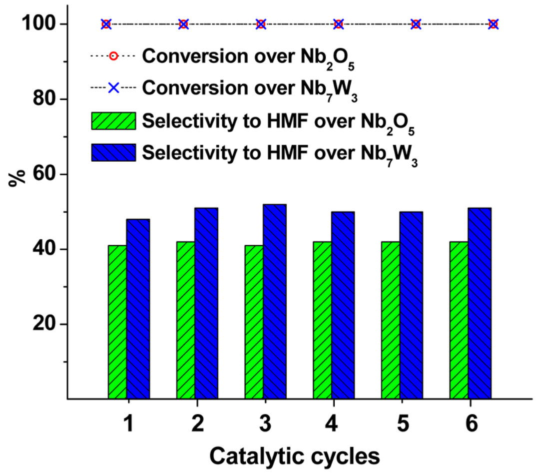


Figure 10 Reuse of Nb_2O_5 and Nb_7W_3 oxide for the conversion of glucose into HMF. 0.2 g of catalyst, 2 mL of 1 wt% *D*-glucose and 5 mL of 2-butanol (2-butanol/H_2O=5∶2, *V*/*V*) were stirred in an autoclave at 140 ℃ for 2 h.

A further investigation of mesoporous Nb and Nb-W oxide along with other relevant catalysts in the conversion of sugars such as glucose, fructose and sucrose into HMF in the 2-butanol/H_2O catalytic system is shown in Table 2. The selectivity of HMF from fructose, which is highly determined by the amount of Brønsted acid sites on catalyst, is in the order of $Nb_2O_5{\bullet}nH_2O \approx Nb_5W_5 \approx Nb_7W_3 > Nb_9W_1 > Nb_2O_5 >$ blank. These results are consistent with the acidity characterization of Nb and Nb-W oxides in this work by solid state ^{31}P MAS NMR and the fact that $Nb_2O_5{\bullet}nH_2O$ has abundance of Brønsted acid sites.

Although there is a well-known fact that keto-hexoses produce higher yields of HMF compared to aldo-hexoses,[62] it is interesting to note that glucose conversion over Nb_2O_5 and Nb-W oxides proceeds higher

Table 2 Results for the conversion of sugars using different catalysts[a]

Substrate	Catalyst	Conversion/mol%	HMF yield/mol%	HMF selectivity/mol%
Fructose	Nb_2O_5	>99	28	28
	Nb_9W_1	>99	33	33
	Nb_7W_3	>99	39	39
	Nb_5W_5	>99	40	40
	$Nb_2O_5 \cdot nH_2O$	>99	42	42
	No catalyst	16	2	13
Glucose	Nb_2O_5	>99	42	42
	Nb_9W_1	>99	47	47
	Nb_7W_3	>99	52	52
	Nb_5W_5	96	44	46
	$Nb_2O_5 \cdot nH_2O$	56	13	23
	No catalyst	15	2	13
Sucrose	Nb_2O_5	>99	36	36
	Nb_9W_1	>99	42	42
	Nb_7W_3	>99	45	45
	Nb_5W_5	>99	46	46
	$Nb_2O_5 \cdot nH_2O$	74	13	18
	No catalyst	31	2	6

[a] Reaction conditions: 0.2 g of catalyst, 2 mL of 1 wt% sugar and 5 mL of 2-butanol (2-butanol/H_2O=5 : 2, *V*/*V*) were stirred in an autoclave at 140 ℃ for 2 h.

HMF selectivity than those from fructose. The results in Table 2 show that the highest selectivity of HMF from glucose is achieved by using Nb_7W_3 oxide catalyst, approaching 52% with almost 100% glucose conversion in comparison with 39% HMF selectivity from fructose in the same reaction conditions. This observation suggests that unselective condensation of fructose and HMF is favored over catalysts with relatively high density of Lewis acid sites such as Nb_2O_5, since only $Nb_2O_5 \cdot nH_2O$ was found to induce higher selectivity of HMF for fructose (42%) than glucose (23%). As for HMF formation from glucose, continuous formation of fructose by glucose isomerization on Lewis acid sites and further dehydration of fructose to HMF on Brønsted acid sites keep the concentration of formed fructose relatively low, which minimizes undesired reaction like cross-polymerization of fructose and HMF or condensation of unreacted fructose on Lewis acid sites. Moreover, when sucrose was employed as the substrate, the conversion of sucrose follows the selectivity trends for the conversion of glucose or fructose, which is due to that sucrose behaves as the 1 : 1 mixture of fructose and glucose. In general, when using Nb_2O_5 and Nb-W oxides as the catalysts, the selectivity of HMF from sucrose is slightly lower than that from glucose under the same reaction conditions because sucrose should be firstly hydrolyzed to form equimolar glucose and fructose. In contrast, $Nb_2O_5 \cdot nH_2O$ with predominant Brønsted acidity does not improve the selectivity of HMF for the conversions of sucrose (18%) and glucose (23%), revealing that isomerization of glucose is the rate-determining step for HMF formation. This result is in agreement with the work of Domen and co-workers,[54] where they found niobic acid showed low activity in sucrose hydration.

In all cases, the sugar conversion and the selectivity of HMF without catalyst achieve the minimum value, indicating that the solid acid catalyst plays a pivotal role in HMF formation from sugar. Mesoporous Nb and Nb-W oxides show effective catalytic activities for HMF formation from sugars such as glucose, fructose and sucrose. Furthermore, it reveals that the 2-butanol/H_2O catalytic system with acid Nb-W oxide catalysts could also be applied in the direct formation of HMF from other inexpensive and abundantly available renewable feedstocks through their hydration to monosaccharides.

Conclusions

In summary, a series of mesoporous Nb and Nb-W oxides were prepared and employed as highly catalytic active, recyclable solid acid catalysts for the conversion of glucose to HMF. Solid state ^{31}P MAS NMR spectroscopic study with TMP as the probe molecule reveals that the addition of tungsten in niobium oxide increases the number of Brønsted acid sites and decreases the number of Lewis acid sites.

The dehydration of glucose in aqueous medium is achieved by tandem reactions including isomerization of glucose to fructose over Lewis acid sites and fructose dehydration to HMF over Brønsted acid sites. The catalytic activity and selectivity for all Nb-W oxides vary according to the ratios of Brønsted to Lewis acid sites. Higher glucose conversion was achieved over Nb$_5$W$_5$ and Nb$_7$W$_3$ oxides with relatively high ratios of Brønsted to Lewis acid sites.

The selectivity of HMF can be further improved with a 2-butanol/H$_2$O system. The organic phase may extract formed HMF from the aqueous phase, thus suppressing HMF rehydration and condensation, leading to high stable catalytic activity of Nb and Nb$_7$W$_3$ oxides. Among those catalysts studied, Nb$_7$W$_3$ oxide exhibits ＞99% conversion of glucose and 52% HMF selectivity. Moreover, this catalytic system can also be extended to conversion of sucrose, achieving high HMF selectivity of 45%—46% over Nb$_7$W$_3$ and Nb$_5$W$_5$ oxides.

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