Direct conversion of biomass-derived carbohydrates to 5-hydroxymethylfurural over water-tolerant niobium-based catalysts

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HIGHLIGHTS

- One-pot conversion of glucose to HMF in aq. solution can be realized with high yield.
- Mesoporous $NbOPO_4$ with tunable acidity and L/B acid ratio was synthesized.
- Lewis acid played a key role in the isomerization of glucose to fructose.
- More Lewis acid would lead to the formation of humins in the next dehydration step.
- The balance between L/B acid types is important for the conversion of glucose to HMF.

GRAPHICAL ABSTRACT
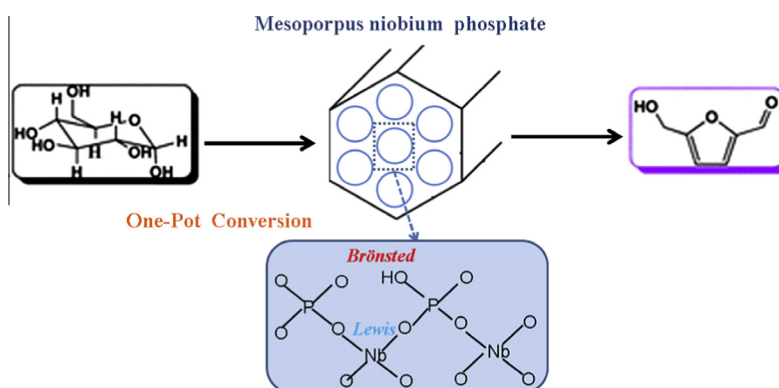
ABSTRACT

A series of water-tolerant porous niobium phosphate solid acid catalysts were hydrothermal synthesized using cetyltrimethyl ammonium bromide (CTAB) as the template. The tuning of surface acidity and the ratios of acid types (Brönsted and Lewis acid sites) was realized by adjusting the pH values in synthetic processes. It was found that the acidic properties and the balance between Brönsted/Lewis acid types of solid acid catalysts had great influence on the selective conversion of glucose or glucose-united carbohydrates, such as sucrose, cellobiose, starch and cellulose into 5-hydroxymethylfurural (HMF) in pure water. It is found that Lewis acid sites played an important role in the isomerization of glucose into fructose, whereas excessive Brönsted acid sites had detrimental effect on this isomerization process; Brönsted acid sites were active for further dehydration of generated fructose to HMF, but excessive Lewis acid would lead to the formations of by-products (e.g., humins) and decrease the selectivity to HMF. Under optimal reaction conditions, as high as 33.2% yield of HMF can be obtained from glucose in pure water over porous niobium phosphate catalyst synthesized at pH = 7. The yield of HMF can be slightly increased to 39.3% in a biphasic water/methyl isobutyl ketone medium. Furthermore, this catalyst also displayed excellent performances on the conversion of other carbohydrates and exhibited high recycle stabilities.

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1. Introduction

In order to establish the eco-friendly chemical processes for sustainable industries, great efforts have been made for the utiliza-

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tion of renewable biomass resources. Sugars (glucose, xylose, etc.) as the derivatives of lignocellulosic biomass are important feedstock for the production of energy, fuels and chemicals, such as furan-based compounds [1,2]. Among these furan compounds [3–5], 5-hydroxymethylfurural (HMF), has been extensively studied as it can serve as chemical platform molecule for the production of liquid fuels and valuable fine chemicals [6,7]. Although HMF can be easily obtained from fructose with high yield in organic or aqueous system [8–10], the cost of using fructose as raw material is huge, because the enzymatic isomerization of glucose syrup, which is employed for fructose production in industrial process, requires an expensive chromatographic step to achieve the desired fructose concentration [11]. So if glucose or glucose-based carbohydrates can be used as the raw material directly, the industrial process for the production of HMF would be much more economical and beneficial.

The challenge of using glucose as a raw material is the high stability of the glucose ring, which makes the dehydration process quite difficult. It has been reported that the conversion of glucose into HMF could proceed in two steps: the first isomerization of glucose to fructose catalysed by enzyme, Lewis acid or base catalysts, followed by the dehydration of generated fructose to HMF in acidic conditions. Although many enzymatic and alkaline systems can be used to catalyze the isomerization of glucose [12,13], few can be directly applied into one-pot production of HMF due to the absence of acidic media in the second dehydration step. Common Lewis acid, such as $CrCl_2$ or $SnCl_4$ has exhibited excellent performances for the isomerization of glucose into fructose and further dehydration of generated fructose in ionic liquid solvent, and the yield of HMF was in the range of 60–70% [14,15]. However, the chromium ions is toxic and the process for the recycling of $SnCl_4$ is still a problem. Alternatively, Davis et al. found that Sn-Beta could efficiently catalyze the isomerization of glucose to fructose and the generated fructose can be converted to HMF rapidly with the aid of hydrochloric acid [16,17]. However, for the synthesis of Sn-beta, a certain amount of hydrofluoric acid (HF) must be used. HF is highly corrosive, noxious, easy to volatilization and very harmful to human and environment, which makes this synthetic process less eco-friendly. Besides, single Sn-beta catalyst was only active for the isomerization of glucose to fructose, so external acidic catalyst, such as HCl or Amberlyst-15, is needed to convert the generated fructose to HMF. This means that the co-existence of Brönsted and Lewis acid sites is necessary for the efficient conversion of glucose to HMF in one-pot catalytic system.

Recently, Wang et al. [18] easily prepared a cheap Sn-Mont catalyst via the ion-exchange method. This catalyst with suitable ratio of Brönsted to Lewis acid sites exhibits excellent activity in dehydration of glucose to HMF in organic solvents or biphasic system. However, such catalyst has lower activity in pure water, since water at high reaction temperature may deactivate most solid acid catalysts. Compared to organic or ionic liquid solvents, water is a green and convenient reaction medium with remarkable advantages, especially increasing the economic feasibility to product HMF in large scale. Herein, design a novel catalytic material with better properties of water-tolerance and suitable ratio of Brönsted to Lewis acid sites, particularly at high temperature is still a challenge.

Niobium-based materials have been identified as solid acids with excellent water-resistant properties [19–21]. Yang et al. [22] have investigated the dehydration of glucose into HMF by using H_3PO_4-modified Nb_2O_5 (NA-p) as catalyst in a biphasic water/2-butanol system, and 49.0% yield of HMF was obtained at high temperature. Nijhuis et al. [23] have investigated the dehydration of glucose over aluminum (AlPO), titanium (TiPO), zirconium (ZrPO), and niobium phosphates (NbPO) catalysts, and found that the selectivity to 5-hydroxymethylfurfural (HMF) was dependent on the ratio of Brönsted and Lewis acid sites. However,

for niobium-based materials, to the best of our knowledge, there was no report about the available tuning of the acid types and distribution on the surface although they have been investigated as water-tolerant solid acid catalysts in dehydration, alkylation and esterification reactions [24]. In our previous work, we found that mesoporous niobium phosphate catalyst had both Brönsted and Lewis acid sites and exhibited high activity in the dehydration of fructose to HMF in pure water [25]. Here, we further adjusted the acidic properties, the ratios of Brönsted to Lewis acid sites and the total acid amounts of these mesoporous niobium phosphate catalysts, and investigated their activities for the direct conversion of glucose to HMF in pure water. Furthermore, the conversions of other glucose-united carbohydrates, such as sucrose, cellobiose, starch and cellulose into HMF were also investigated in this catalytic system.

2. Experimental section

2.1. Chemicals

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd, and Nb tartrate was prepared in our laboratory according to the literature [25,26]. All bought chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis of mesoporous niobium phosphate (NbPO) and Nb_2O_5

Mesoporous niobium phosphate catalysts at different values of pH were prepared according to our previous work [25]. In a typical synthesis, 1.32 g (0.01 mol) of diammonium hydrogen phosphate was dissolved in 20 mL water, and then the mixture was adjusted at pH = 2 using phosphoric acid. Under vigorous stirring, 20 mL of 0.5 M niobium tartrate (pH = 2) was added to the above solution. Then the mixed solution was dropped into the aqueous solution of CTAB, which was previously prepared by dissolving 1.0 g of CTAB in 13 mL of water. The pH value of the final solution was about 2. Afterwards, this mixture was stirred for additional 60 min at 35 °C, and then the solution was aged in a Teflon-lined autoclave for 24 h at 160 °C. After cooled down, the solid was filtered, washed with distilled water and then dried at 50 °C. Finally, NbPO-pH2 sample was obtained by calcination at 500 °C for 5 h in air to remove organic species. Similarly, another two NbPO samples were also synthesized using the above mentioned approach, but at different initial pH values. For sample NbPO-pH7, diammonium hydrogen phosphate and niobium tartrate were just mixed together. For NbPO-pH10 sample, the solutions of diammonium hydrogen phosphate and niobium tartrate were adjusted to pH = 10 by using aqueous ammonia, respectively, and then they were mixed together to serve as precursor. Other treatments were the same as NbPO-pH2 sample.

The synthesis of mesoporous Nb_2O_5 was similar to that of NbPO except addition of ammonium phosphate, where only water was added to previous niobium tartrate to get the final precursor.

Na–NbPO-pH7 sample was obtained by ion-exchange of NbPO-pH7 sample with Na$^+$. In details, 3.0 g of NbPO-pH7 sample was stirred in 300 mL of 0.2 M NaCl solution, and the mixture was maintained at pH = 5.5 by adding 0.05 M NaOH solution. After 24 h, the collected sample was washed repeatedly with distilled water until Na$^+$ and Cl$^-$ ions were no longer detected, and then dried at 373 K for 24 h.

2.3. Characterization

Powder XRD patterns were recorded on a Bruker diffractometer (D8 Focus) by using Cu Kα (λ = 0.15406 nm) radiation. Nitrogen