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Journal:	<i>Green Chemistry</i>
Manuscript ID:	GC-ART-02-2015-000440.R2
Article Type:	Paper
Date Submitted by the Author:	19-May-2015
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ARTICLE

Production of methyl levulinate from cellulose: the selectivity and mechanism study

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Cite this: DOI: 10.1039/x0xx00000x

The alcoholysis of cellulose into methyl levulinate (ML) in methanol media was investigated in the presence of several kinds of acid catalysts. One of the synthesized solid niobium-based phosphate catalysts was found to be highly efficient for the generation of ML, with the ML yield reached as high as 56%, higher than LA yield (52%) in aqueous solution at the same reaction conditions in our previous study (Green Chem. 2014, 16, 3846–3853). More interestingly, in water, the higher strong Lewis acid promoted the formation of LA; but in methanol, it is Brønsted acid, which enhanced the formation of ML. Deep investigation showed that the mechanism and type of intermediates of cellulose alcoholysis in methanol were different from those in water and a high Brønsted/Lewis acid ratio (known as B/L acid ratio) of solid catalysts is needed to prevent the generation of by-products, namely, methyl lactate and 1,1,2-trimethoxyethane. This new-proposed reaction mechanism affected by the B/L acid ratio was very helpful for the design of efficient catalysts.

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Introduction

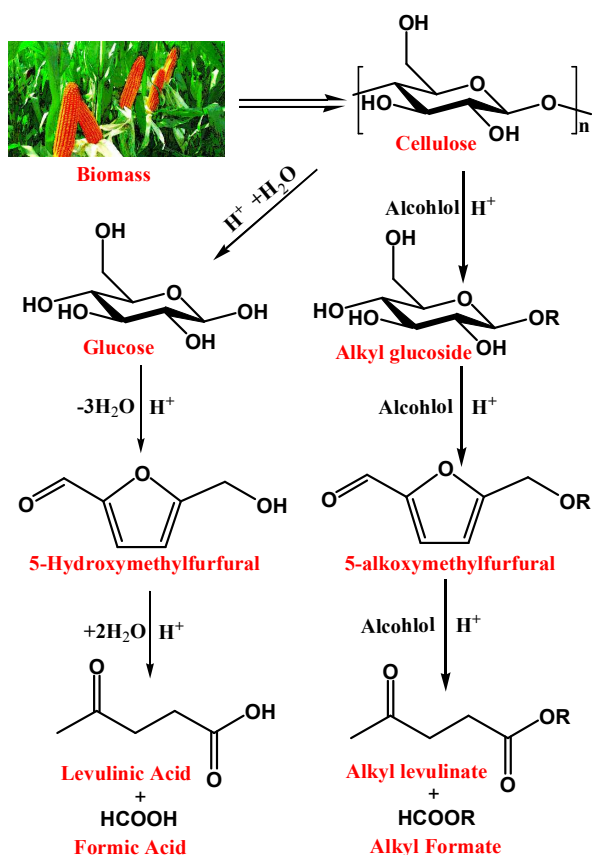
Recently, the abundant and renewable biomass is regarded as a promising alternative to non-renewable resources for the sustainable biofuels and biochemicals due to the deterioration of the environment and inevitable depletion of fossil resources. More and more researches are focused on the production of liquid fuels and high-quality chemicals from the conversion of biomass.^{1,2} In all these explorations, levulinic acid (LA) is one of the most popular derivatives³ converted from carbohydrate, which can be used widely in agriculture, foods, medicines, cosmetics, spice industries and biofuels probably in future. However, due to its high acidity, high viscosity and high boiling point (around 246 °C), the production of LA is limited by the cost of reactor and the separation equipment. As one of the alternatives of levulinic acid, methyl levulinate (ML) gives a better performance in production and separation because it is almost non-corrosive to the reactor, and has a lower boiling point (around 190 °C), indicating lower energy consumption in separation. ML is as useful as LA in many fields, such as medicines, solvent,

organic chemistry⁴, fragrance and furthermore it can be directly used as additives for gasoline and diesel, due to its excellent performances, such as high lubricity, flashpoint stability, non-toxic and better flow properties under cold condition.⁵

Technically, there are three ways to achieve a high selectivity to alkyl levulinate^{6,7}, namely, the esterification of LA^{8,9}, the alcoholysis of 5-(chloromethyl)furfural¹⁰ which was synthesized from biomass in high concentration of hydrochloric acid, and the direct conversion of biomass in alcohol. In industry, the production of levulinate esters were mainly obtained directly from the esterification of LA with alcohols^{8,9}, catalyzed by liquid acid. The alcoholysis of 5-(chloromethyl)furfural¹⁰ can also give a high selectivity to alkyl levulinate (ca. 90%). However, both esterification of LA with alcohols and alcoholysis of 5-(chloromethyl)furfural need a high concentration of liquid acid, which is not environmentally friendly. Therefore, the direct production of levulinate esters from biomass or biomass-based platforms through alcoholysis would be a viable option worth studying.

The generally accepted pathways for the direct conversion of cellulose to LA in water and levulinate esters in alcohol are drawn in Scheme 1. The structure of intermediates in alcohol is different from that generated in water. For example, in water it is followed as cellulose-glucose-HMF-LA pathway, while in methanol, methyl glucoside and 5-methoxymethylfurfural (5-MMF) are formed in sequence, then converted into methyl levulinate.^{10,11}

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Scheme 1 Reaction pathways for the acid-catalyzed conversion of cellulose to levulinate esters in alcohol,^{11,12} compared with that to levulinic acid in water.¹³

In previous reports, sulfuric acid is used as a very efficient catalyst to achieve a high selectivity of methyl levulinate from cellulose alcoholysis directly. For example, Wu *et al.*¹⁴ achieved a 55% yield of methyl levulinate from cellulose, catalyzed by H_2SO_4 . Other liquid acid, including p-toluenesulfonic acid, H_3PO_4 , HCOOH and CH_3COOH was also tested in reaction. Unfortunately, H_3PO_4 , HCOOH and CH_3COOH gave out very low yield of methyl levulinate. The p-toluenesulfonic acid and H_2SO_4 had another serious problem because they were excellent catalysts for methanol etherification, and would making solvent decrease sharply. For example, Peng *et al.*^{11,15} reported that the $-\text{SO}_3\text{H}$ containing solid acid was a very good catalyst for the conversion of methanol to dimethyl ether, which would consume solvent very fast, so they used a series of solid catalysts including $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{Zr}_3(\text{PO}_4)_4$ and Si-Al zeolites to generate methyl levulinate from biomass, and found that $\text{SO}_4^{2-}/\text{TiO}_2$ was a potential catalyst.¹¹ When using glucose as substrate, 35% yield of methyl levulinate was achieved over $\text{SO}_4^{2-}/\text{TiO}_2$. However, when cellulose was used as substrate, the yield of methyl levulinate was only about 10%, which means that the performance of $\text{SO}_4^{2-}/\text{TiO}_2$ catalyst was poor for the production of methyl levulinate from cellulose. Large amount of methyl glucoside and small amount of 5-methoxymethylfurfural (5-MMF) were still existed in the solution. Some similar situations were found when using heteropolyacid and their salts as

catalysts. Rataboul¹⁶ and Deng¹⁷ used $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{20}\text{O}_{40}$, respectively, for the alcoholysis of cellulose in methanol, and both achieved about 20% of methyl levulinate, with large amount of methyl glucoside as main product. The left of the large amount of methyl glucoside in solution means that these catalysts were not active enough to catalyze the further hydration or transformation.

There are some other interesting works to investigate the selectivity to methyl levulinate in cellulose conversion. Tominaga *et al.*¹⁸ investigated the influence of Brønsted/Lewis acid ratio on the alcoholysis of cellulose by using a series of mixed Brønsted/Lewis liquid acids. They found that the mixed Brønsted/Lewis acid system with B/L ratio of 5/1 had a highest selectivity to methyl levulinate (70%), compared to pure Brønsted (20%) or pure Lewis acid (52%), which was never reported before. As far as we know, many kinds of solid acid has both Brønsted and Lewis acid sites, such as $\text{SO}_4^{2-}/\text{ZrO}_2$, metal phosphate and zeolites, except for sulfonic acid resin, so this result might be useful for the design of solid acids in biomass conversion.

Although Tominaga *et al.*¹⁸ had realized the B/L acid ratio will affect the methyl levulinate selectivity, but reasonable mechanism was not given to explain the phenomenon, especially how Brønsted and Lewis acid works on the transform of intermediate, such as, methyl glucoside and 5-methoxymethylfurfural (5-MMF) to methyl levulinate. Learning the details of the transform mechanism on Brønsted and Lewis acid sites will be helpful to enhance the production yield of methyl levulinate.

On the other hand, lactic acid¹⁹, methyl lactate²⁰ and 1,1,2-trimethoxyethane²¹ could also be generated from the break of C-C bond, catalyzed by the Lewis acid sites on solid catalysts. In the production of methyl levulinate, the generation of by-products should always be aware of, for it will consume carbon atoms and compete with the selectivity to methyl levulinate.

In summary, there are several problems to be solved in the conversion of cellulose into methyl levulinate. Firstly, the prevention of methanol etherification; secondly, improving cellulose conversion rate and methyl levulinate selectivity; thirdly, the influence of Brønsted and Lewis acid sites on the intermediate and product selectivity, through analysing the pathway and mechanism in transformation. To solve these problems, a series of solid acid catalysts, including mesoporous niobium phosphate catalysts^{22,23} were used in these studies, and highest yield of 56% methyl levulinate was achieved over mesoporous niobium phosphate prepared at pH1. Moreover, this catalyst has excellent reusability and can be used for 5 times with only slight loss of activity and with little etherification of methanol. The detailed reaction pathway, the product distributions (including intermediates) and the role of Lewis acid in alcoholysis were also investigated in main text.

Experimental Section

Chemicals

All chemicals used here were purchased from Sinopharm Chemical Reagent Co. Ltd, except the cellulose, which was bought from Fluka Analytical Co. Ltd. All bought chemicals were of analytical grade and used without further purification.

Catalysts Preparation

Mesoporous niobium-based phosphate NbP-pH2 was synthesized according to our previous reports^{13,22}. Typically, 0.01 mol of diammonium hydrogen phosphate was dissolved in 20 mL water and adjusted to pH 2 using phosphoric acid, then 20 mL of 0.5 M niobium tartrate (pH = 2) was added to the above solution with stirring. The mixed solution was slowly dropped into the previously prepared aqueous solution of cetyltrimethyl ammonium bromide (CTAB), which containing 1.0g of CTAB and 13ml water, and the final pH was around 2. Large amount of niobium-phosphorus precipitation appeared immediately from the solution and the mixture was stirred for additional 60 min at 35 °C. Then it was transferred into a Teflonlined autoclave and aged at 160°C for 24h. The deposit was filtered after cooling down, washed with distilled water and dried at 100 °C overnight. Finally, the catalyst was obtained by calcination at 500 °C for 5h in air to remove organics.

The NbP-pH1 was synthesized using the identical steps of catalyst NbP-pH2, except the solution of diammonium hydrogen phosphate was adjusted to pH1 by using polyphosphoric acid. The synthesis of aluminum-modified porous niobium phosphate was similar to above procedure except the addition of calculated amount of aluminium precursor, which was prepared by dissolving aluminum hydroxide in 10mL of 1.5 M oxalic acid solution and then added into the mixed solution with stirring.

Characterizations

The pyridine adsorption infrared (IR) spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, with 32 scans at an effective resolution of 4cm⁻¹. Around 50mg of the catalyst was pressed into a self-supporting disk and placed in an IR cell attached to a closed glass-circulation system. The catalyst disk was dehydrated by heating at 400°C under vacuum in order to remove physis-adsorbed mixtures. The IR spectrum background was recorded at room temperature when the cell cools down. Pyridine vapour was then introduced into the cell at room temperature until equilibrium was reached. Subsequent evacuations were performed at 100 °C for 60 min followed by spectral acquisitions at room temperature using the background recorded before. The acid sites amounts of catalysts were calculated from pyridine adsorption integral curve recorded.

The BET properties of porous catalysts were calculated from Nitrogen adsorption-desorption isotherms measured at -196 °C on a NOVA 4200e analyser (Quantachrome Co. Ltd). All samples were outgassed at 180 °C for 12 h under vacuum to remove moisture and volatile impurities before the measurements.

Catalytic reactions

A batch reactor was used in the conversion of cellulose to levulinic ester. Typically, the mixture of 0.0004 mol acid catalyst, 0.5 g cellulose, 0.5 g water and 9.5 g methanol was loaded into a Teflon-lined stainless steel autoclave and placed into a temperature-controlled electric heating mantle with a thermocouple probed detector and magnetic stirring. N₂ was used as a protective gas and kept at a pressure of about 0.8 MPa. The zero time was taken when

the Teflon-lined stainless steel autoclave was placed into the heating mantle under magnetic stirring, which had already been heated to the set temperature. After reaction, the solid catalyst was collected by centrifugation and washed by water and ethanol for several times, then dried at 100 °C for 24 hours for next run.

The analysis of reaction mixture was carried out by HPLC (Agilent 1200 Series) and GC7890-MSD. The former was equipped with an ion-exclusion column Aminex HPX-87H(Bio-Rad), eluting with an aqueous solution of sulphuric as mobile phase. The products and intermediates were analyzed with a refractive index detector (Agilent G1362A) in the HPLC to complete the quantitative analysis. All the intermediates were also separated by GC7890 which using high purity helium as carrier gas, and the molecular structure were analyzed qualitatively by the MSD connected with GC.

Cellulose remained in solid mixture was analyzed by weighing method, for it could be dissolved quickly and completely in hot sulfuric acid solution, meanwhile the catalysts and humins were 100% insoluble. So after the reaction, the solid mixture was dry and weighed for the first round, then soaked into the 0.5 mol·L⁻¹ of sulfuric acid solution, heated to 160 °C for 6 hours, to make sure the cellulose was completely dissolved. The rest of the solid mixture was washed, dried and weighed for a second round. Comparing the data from two weighing rounds the cellulose conversion could be calculated with high precision. The humins dissolved in methanol solution was also weighed and quantitated^{25,26} after methanol and small molecules was removed in 100°C for 12 hours.

Results and Discussion

Performance and products distribution of various catalysts in the alcoholysis of cellulose

Normally, in the alcoholysis of cellulose to levulinic acid, Brønsted acid was used. Here mesoporous niobium phosphate synthesized at pH 1 was used in the alcoholysis of cellulose, along with other catalysts used in conversion of cellulose to LA in water.¹³ Table 1 summarized their physical and acidic properties, the N₂ adsorption-desorption isotherm and Py-FTIR spectrum were provided in supporting information. For comparison, hydrochloric acid, trifluoromethanesulfonic acid (a strong Brønsted acid), H-beta (Si/Al=50) and (TfO)₃Yb (Lewis acid) were also used by controlling the total acid amount of 0.0004 mol. The yields of methyl levulinate as well as other products were presented in Figure 1. Except (TfO)₃Yb, a Lewis acid, cellulose conversion over all other catalysts were higher than 95%, even though the products distribution was different. In these catalysts, the performance of NbP-pH1 prepared with the precursor mixture of pH=1 was much better than any other solid acids reported here and before^{11,14-17} and almost as excellent as soluble acid catalyst (hydrochloric acid), giving a 56% yield of methyl levulinate. This provides a possibility to produce methyl levulinate from cellulose over solid acid catalyst, which can prevent the neutralization of liquid acid. The yield of methyl levulinate (14.7%) over H-beta was also reasonable for its small pore size (less than 1nm), which will lead to mass transfer limitation and coke

formation, in accordance with the results reported before.²⁴ The interesting thing was that Al-NbP-pH2, an excellent catalyst in the production of LA from cellulose in water²², was very poor for the formation of methyl levulinate. The yield of methyl levulinate is only 25%, and more carbon was in by-products such as 1,1,2-trimethoxyethane and 5-methoxymethylfurfural (5-MMF), indicating the different pathways in water and alcohol.

Table 1 Physical and acidic properties (Py-FTIR at 373 K) of various solid acids.

Catalyst	S _{BET} /m ² g	Pore size /nm	Brønsted acid/μmol·g ⁻¹	Lewis acid/μmol·g ⁻¹	B/L acid ratio
H-Beta	501.1	0.50	1125.0	645.6	1.74 / 1
NbP-pH1	152.0	3.9	850.8	359.2	2.15 / 1
NbP-pH2	233.0	3.8	641.5	345.1	1.86 / 1
Al-NbP-pH2	50.0	9.6	492.6	469.3	1.05 / 1
Element	Nb/at%	P/at%	Al/at%	O/at%	
NbP-pH1	15.1	20.7	—	64.2	
NbP-pH2	20.9	21.0	—	58.1	
Al-NbP-pH2	17.4	18.6	2.49	61.5	

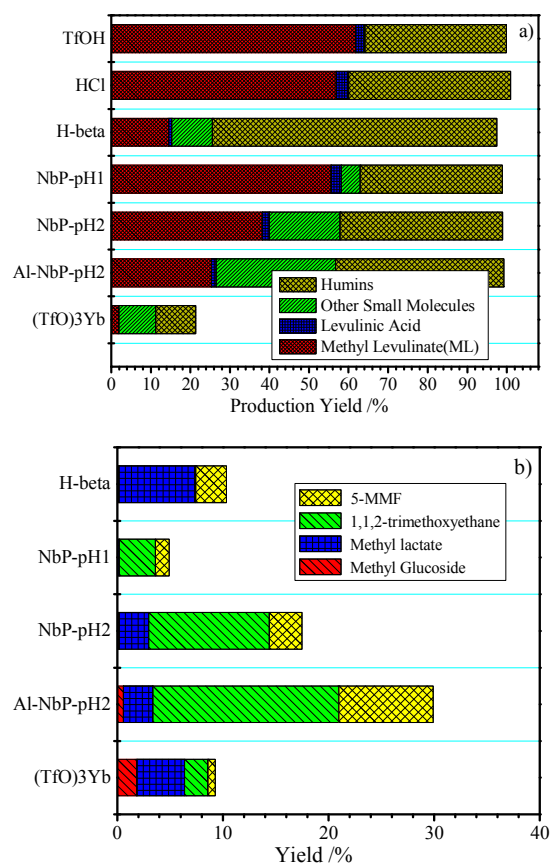
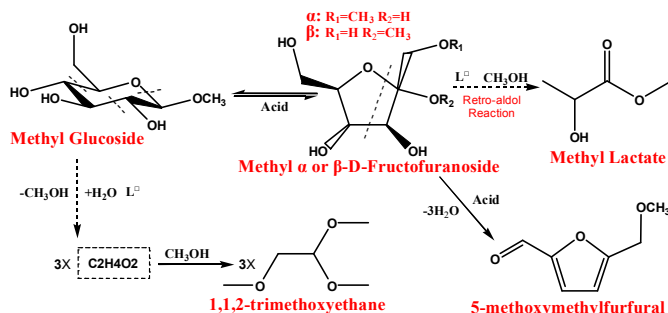


Fig. 1 (a) Catalytic performance of various catalysts in the conversion of cellulose; (b) the detailed distribution of other small

molecules, green part in (a). Reaction conditions: 0.5g of cellulose, 0.0004mol of acid catalysts, 10 g of 95% methanol, 180 °C, 24 h.

Normally, in the alcoholysis of cellulose to levulinate, Brønsted acid was used. Here mesoporous niobium phosphate synthesized at pH 1 was used in the alcoholysis of cellulose, along with other catalysts used in conversion of cellulose to LA in water.²³ Table 1 summarized their physical and acidic properties, the N₂ adsorption-desorption isotherm and Py-FTIR spectrum were provided in supporting information. For comparison, hydrochloric acid, trifluoromethanesulfonic acid (a strong Brønsted acid), H-beta (Si/Al=50) and (TfO)₃Yb (Lewis acid) were also used by controlling the total acid amount of 0.0004 mol. The yields of methyl levulinate as well as other products were presented in Figure 1. Except (TfO)₃Yb, a Lewis acid, cellulose conversion over all other catalysts were higher than 95%, even though the products distribution was different. In these catalysts, the performance of NbP-pH1 prepared with the precursor mixture of pH=1 was much better than any other solid acids reported here and before^{11,14-17} and almost as excellent as liquid acid catalyst (hydrochloric acid), giving a 56% yield of methyl levulinate. This provides a possibility to produce methyl levulinate from cellulose over solid acid catalyst, which can prevent the neutralization of liquid acid. The yield of methyl levulinate (14.7%) over H-beta was also reasonable for its small pore size (less than 1nm), which will lead to mass transfer limitation and coke formation, in accordance with the results reported before.²⁴ The interesting thing was that Al-NbP-pH2, an excellent catalyst in the production of LA from cellulose in water²², was very poor for the formation of methyl levulinate. The yield of methyl levulinate is only 25%, and more carbon was in by-products such as 1,1,2-trimethoxyethane and 5-methoxymethylfurfural (5-MMF), indicating the different pathways in water and alcohol. During the analysis of GC-MS and HPLC data, we found that except the intermediates, methyl glucoside and 5-methoxymethylfurfural drawn in Scheme 1 and found in Figure 1a, there were other two by-products from the C-C bond break of methyl glucoside, known as methyl lactate and 1,1,2-trimethoxyethane, shown in Figure 1b over various solid acid catalysts. These catalysts all have large amount of Lewis acid sites. As we know that methyl glucoside was always the intermediate during the alcoholysis of cellulose,²¹ it can be transformed through different ways: i) direct dehydration to 5-MMF, following by hydration to methyl levulinate; ii) C-C cleavage through retro-aldol condensation catalyzed by Lewis acid directly or iii) through methyl fructoside, the possible pathways over Lewis acid is drawn in Scheme 2. In the production of lactic acid and alkyl lactate from biomass,^{19,20} the breakage of C-C bond always occur when enough Lewis acid exists in solution, thus making the levulinate species and lactate species co-existed here. It was found from Figure 1 and Table 1 that the catalyst containing higher Lewis/ Brønsted acid ratio would give a higher yield of methyl lactate/1,1,2-trimethoxyethane and lower methyl levulinate yield. To further understand the generation of these small molecules and the influence of Lewis acidic sites, a deeper investigation was done.



Scheme 2 Three kinds of reaction pathways of methyl glucoside in methanol.

Generation of other small molecules and their relationships with the acid sites of catalysts

As methyl glucoside was always the intermediate during the alcoholysis of cellulose, and then converted into different species over different kinds of catalysts, so the products distribution during methyl glucoside conversion in methanol over different acid catalysts were carried out. Among the three species listed in Scheme 2, methyl lactate and 1,1,2-trimethoxyethane would not be converted into other species once generated, but as the intermediate, 5-MMF were capable of being transformed into methyl levulinate or still remained in the reaction solution if there was not enough/suitable catalytic active sites on catalysts. Using methyl glucoside as substrate, the change of products distribution over different catalysts was much more obvious than that using cellulose as substrate, as shown in Figure 2. For example, over NbP-pH1 and Al-NbP-pH2 catalysts, the total yield of 5-MMF, methyl lactate and 1,1,2-trimethoxyethane was 13.6 and 54.3%, respectively, while it was 4.79 and 30.2% when using cellulose as substrate. These results give us a proof that our niobium-based phosphate acid catalyst with high Lewis acid ratio is not suitable for the high selectively production of methyl levulinate from biomass.

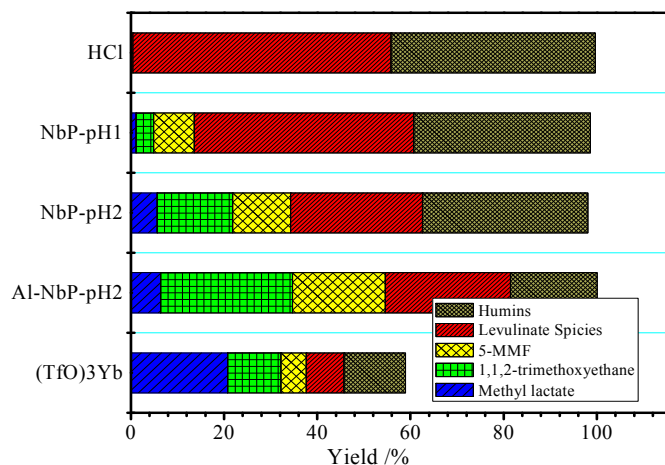


Fig. 2 The products distribution from different acid catalysts in the conversion of methyl glucoside. The reaction condition was same as that in Figure 1.

For the degradation of β -1,4-glycosidic bond in cellulose is the slowest step in the reaction and MS spectra (supporting information, Figure S6) also showed that methyl glucoside was the only compound at the very beginning of the reaction, so as an alternative of cellulose, methyl glucoside can be used as a substrate for further investigation. Figure 3 shows the two time-yield reaction curves in methanol catalyzed by NbP-pH1 and Al-NbP-pH2, respectively, using methyl glucoside as substrate. Actually, the two curves described the detailed performance of two catalysts in Figure 2. It can be seen that over NbP-pH1 catalyst, 5-MMF and methyl levulinate appeared simultaneously at the very beginning of reaction, then 5-MMF increased, reached maximum and decreased again, but methyl levulinate always increased with the prolonging of reaction time. It means that the conversion speed of 5-MMF was slower than that of methyl glucoside, thus made the 5-MMF first accumulated and then consumed slowly. While in all time profile, the yield of alkyl lactate and 1,1,2-trimethoxyethane kept in lower level, indicating more Brønsted acid prevented the C-C bond cleavage. Very differently, over Al-NbP-pH2 catalyst, the yield of 1,1,2-trimethoxyethane was always higher than that of methyl levulinate, reached ca. 31% after reaction for 24h, indicating Lewis acid is favour for the formation of 1,1,2-trimethoxyethane through C-C cleavage. Furthermore there was still 20% of 5-MMF left in solution, indicating the lower reactivity of 5-MMF over Lewis acid.

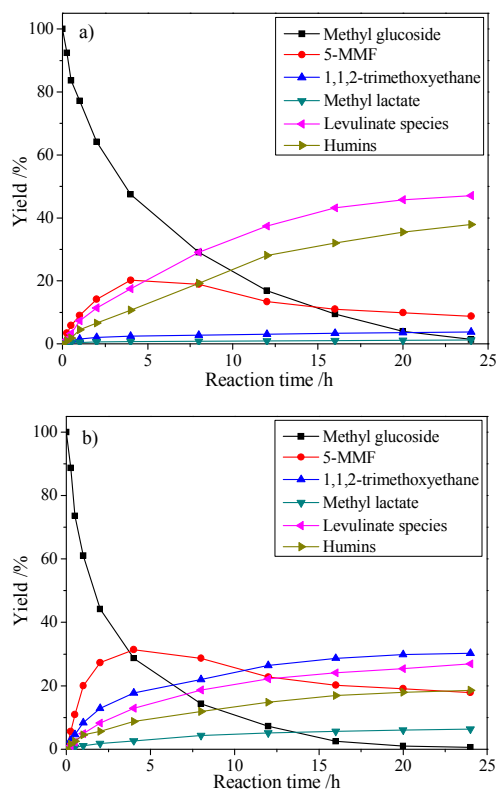


Fig. 3 Time profiles of methyl glucoside conversion over a) NbP-pH1, b) Al-NbP-pH2 catalysts. The reaction condition was same as that in Fig. 1.

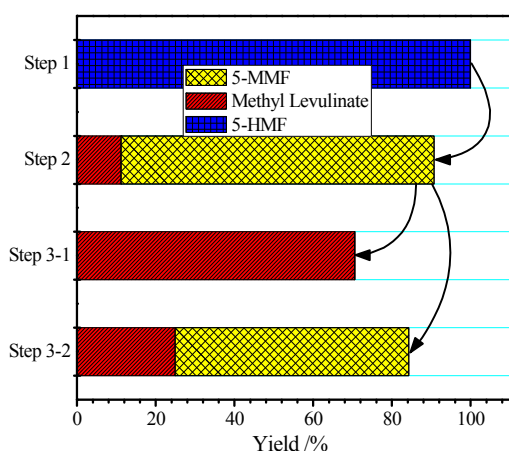
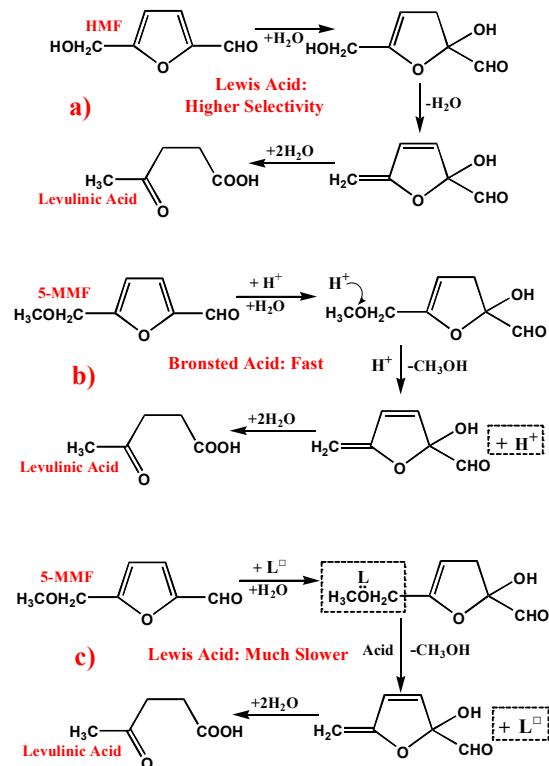


Fig. 4 Step 1) 0.0004mol Al-NbP-pH2 and 0.389g HMF in methanol; Step 2) Solution in Step 1 was heated at 180 °C for 6h; Step 3-1) 0.0008mol HCl and the solution in Step 2 was heated for another 24h at 180 °C; Step 3-2) 0.0008mol Al-NbP-pH2 and the solution in Step 2 was heated for another 24h at 180 °C.

To prove this assumption on 5-MMF conversion, a confirmatory reaction was carried out by using 5-MMF as substrate. Awkwardly, we cannot find a pure 5-MMF reagent, so we choose HMF as an alternative to synthesize 5-MMF in methanol, then investigate its further reaction. First, 0.0004mol of Al-NbP-pH2 catalyst was added into the methanol solution of HMF (step 1 in Figure 4), then reacted at 180 °C for 6h (step 2 in Figure 4), it is found that HMF was completely consumed and generated 79.5% of 5-MMF (Figure S5) and 11.2% of methyl levulinate. Finally, the reaction was further going by adding 0.0008mol HCl (protonated acid, step 3-1 in Figure 4) or 0.0008mol Al-NbP-pH2 (step 3-1 in Figure 4) and heated for another 24h at 180 °C. The results showed clearly that the conversion rate of 5-MMF catalyzed by Brønsted acid was much higher than that by Lewis acid. With HCl, 5-MMF was completely converted after 24h, while over Al-NbP-pH2 solid acid, only 20.1% of 5-MMF was converted.

Looking back to our previous studies,²³ the LA selectivity from HMF increased with the stronger Lewis acid, which seems to be conflict with the results in this work. However, according to the Lund's work,²⁵ the conversion from HMF to LA is not a one-step reaction, there are several active intermediates existed between HMF and LA. We believe that the active intermediates existed between 5-MMF and methyl levulinate in methanol are different from those in water, and it is the reactivity of these active intermediates controlling the rate of 5-MMF conversion with Brønsted acid or Lewis acid. For the first elementary reaction of HMF and 5-MMF, a water molecule is added onto the $-C_{(2)}=C_{(3)}$ - double bond on furan ring, made it have three substituent groups on one furan ring (Scheme 3a and b, first step). For HMF conversion, the second step is the rearrangement of C=C double bonds and dehydration of the molecule, the HOH_2C -substituent group turn into $H_2C=$ and one water molecule is released into solution, which can be catalyzed by Brønsted acid or Lewis acid, as drawn in Scheme 3a, second step.



Scheme 3 Comparison of different mechanisms between hydration of a) 5-HMF and alcoholization of b) 5-MMF catalyzed by Brønsted and Lewis acid catalysts.

While for the second elementary reaction step of 5-MMF, the situation is changed because there is not HOH_2C - substituent group, but H_3COH_2C - group existed in the molecule. Once a water molecule is added onto the $-C_{(2)}=C_{(3)}$ - double bond and $H_2C=$ is generated, a CH_3OH molecule can be released into the solution over Brønsted acid sites through dealcoholization reaction (Scheme 3b, step 2), then lead to the formation of ML. While over Lewis acid catalyst, the catalyst will be coordinated with the lone pair electrons of oxygen atom, then methanol molecule is dissociated into the solution. The whole steps of coordination-dissociation reaction is much slower than the process of being attacked by protons and break the C-O-C bond, so the conversion of 5-MMF catalyzed by Lewis acid is much slower than that by Brønsted acid. Thus the high Brønsted acid/Lewis acid ratio is favourable for the formation of methyl levulinate.

Although the Lewis acid seems no benefit for the production of methyl levulinate from cellulose, but it can enhance the reaction rate of cellulose in methanol. Figure 5 shows the cellulose conversion over different catalysts in the first 6 hours. Two kinds of liquid acid catalysts and two kinds of solid acid catalysts were used for comparison. It can be seen that no matter over liquid or solid acid, the catalyst with more Lewis acid get a higher cellulose conversion rate. As we know, there are multistage structures existed in cellulose, including the long chains made of anhydroglucose units (AGU), the hydrogen bond between AGU chains and the network of long chains. Obviously, the coordinate property of Lewis acid is benefit for the loose of network and break of hydrogen bond in the cellulose; it

speeds up the degradation process from insoluble cellulose to soluble polysaccharides and methyl glucoside.

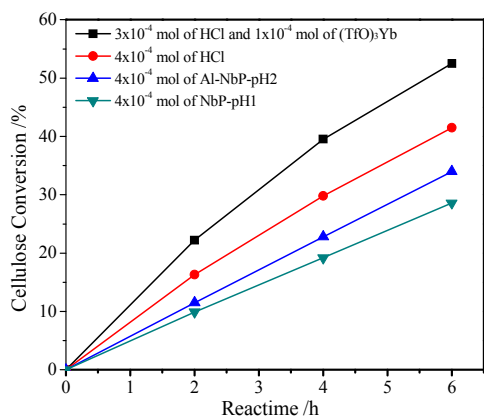


Fig. 5 Comparison on cellulose conversion rate catalyzed by different Brönsted/Lewis acid up to 6h, under the same reaction condition in Fig.1

Reusability and regeneration of NbP-pH1 catalyst

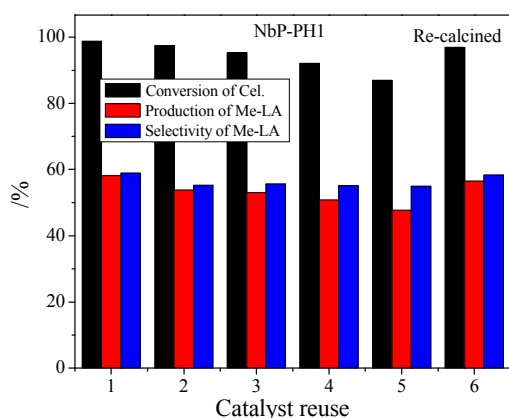


Fig. 6 The stability and regeneration performance of niobium-based phosphate catalyst under the same reaction conditions as that of Fig.1. 0.5g of cellulose, 0.0004mol of acid catalysts, 10 g of 95% methanol, 180 °C, 24 h.

Table 2 Physical and acidic properties (Py-FTIR at 373 K) of recycled NbP-pH1 after five runs.

Catalyst	S_{BET} /m ² g	Pore size /nm	Brönsted acid/μmol·g ⁻¹	Lewis acid/μmol·g ⁻¹	B/L acid ratio
NbP-pH1	131.2	3.9	752.4	372.5	2.02 / 1
Element	Nb/at%	P/at%	Al/at%	O/at%	
NbP-pH1	16.4	19.3	—	64.3	

For the use of solid acid in biomass reaction, the stability and recyclability of catalyst are very important. There will always be formation of humins in the conversion process of sugar and furfural species, and these polymers will cover the surface of solid acid,

made the activity of catalyst decrease very fast. While in methanol, the stability of NbP-pH1 catalyst was excellent as shown in Figure 6. After five runs, the conversion of cellulose and yield of methyl levulinate were decreased ca. 10 and 17% (from 98% and 57% down to the 87.1% and 47.7%) respectively, much better than those in water²¹. The decrease of selectivity would come from some humins formation for it is well accepted that humins in solid will cover the acid sites. The properties of recycled NbP-pH1 catalyst after five runs are listed in Table 2. The BET surface area, acid amount and P content decreased a little bit, but not too much, indicating the stability of the catalyst. After regeneration by calcinations, conversion of cellulose and the yield of methyl levulinate were recovered, up to 97% and 56%, respectively. Considering the environmentally friendly and the excellent reusability, it can be said that the niobium phosphate catalyst is an appropriate option for the catalytic conversion of biomass into methyl levulinate.

Conclusions

This study presented an efficient and environmental friendly catalytic process for the production of methyl levulinate through cellulose alcoholysis over niobium phosphate catalyst. A high yield of methyl levulinate of 56% was achieved from the conversion of cellulose in methanol solution, which is the highest over solid acid catalysts till now. The formation of methyl levulinate through cellulose alcoholysis follows the sequence: cellulose → methyl glucoside → 5-MMF → methyl levulinate, methyl glucoside and 5-MMF are important intermediates and their further conversion is affected by the types of acid. Brönsted acid favours the conversion of methyl glucoside to 5-MMF and then to methyl levulinate; while Lewis acid favours the C-C bond cleavage and prevent the further conversion of 5-MMF. But the co-existence of Lewis acid can promote the hydrolysis of cellulose to glucose or alcoholysis of cellulose to methyl glucoside, thus makes NbP-pH1 with high Brönsted/Lewis acid ratio are excellent catalyst here.

Acknowledgements

This project was supported financially by the NSFC of China (No. 21273071), the Science and Technology Commission of Shanghai Municipality (13520711400, 13JC1401902, 10dz2220500) and the Fundamental Research Funds for the Central Universities, China.

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