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PAPER

# Direct conversion of carbohydrates to 5-hydroxymethylfurfural using Sn-Mont catalyst

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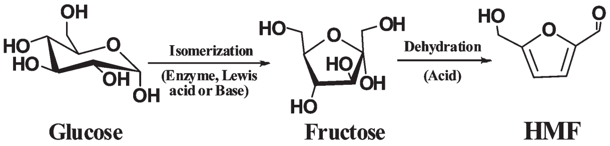
5-Hydroxymethylfurfural (HMF) is a very important intermediate in the fine chemical industry. This study aims to investigate the direct conversion of glucose or glucose-based carbohydrates, such as sucrose, cellobiose, inulin, starch and cellulose, to HMF by using a Sn-Mont catalyst. With the use of this catalyst, a HMF yield of 53.5% was achieved from glucose in a mono-phase medium of tetrahydrofuran (THF)/dimethylsulfoxide (DMSO) at 160 °C for 3 h. The success of one-step conversion of glucose to HMF is attributed to the Sn-Mont catalyst containing two types of acid sites, Lewis acid and Brønsted acid sites. The former one plays a crucial role in the isomerization of glucose to fructose and the latter one is active in the dehydration of generated fructose to HMF. Furthermore, Sn-Mont catalyst also demonstrated excellent activity in the conversion of disaccharides and polysaccharides and as high as 39.1% HMF was directly obtained from cellulose in a THF/$H_2O$–NaCl bi-phasic system.

## 1. Introduction

The conversion of sustainable biomass resources is currently regarded as the most interesting processes for the production of fuels and chemicals to satisfy the anxious need of our industrial society. 5-Hydroxymethylfurfural (HMF), which is one of the most versatile and important building blocks obtainable from biomass, is now considered as a promising candidate for the production of various non-petroleum valuable chemicals and fuels through specific catalytic transformation.[1–5]

Traditionally, HMF is produced by acid-catalyzed dehydration of mono-saccharides, such as fructose or glucose. Since the ring structure of glucose is more stable than that of fructose,[1b] much more satisfying results are obtained from fructose as the reactant catalyzed by homogeneous or heterogeneous acid catalysts. Dumesic *et al.* has reported that about 70% yield of HMF was obtained from fructose in a biphasic system catalyzed by hydrochloric acid.[3a] As we know, homogenous acids are inexpensive and act as high activity for the acid-catalyzed dehydration reactions, but they have the drawbacks in terms of separation and recycling in addition to the equipment corrosion. Shimizu *et al.* reported that 100% HMF yield can be obtained in DMSO with improved removal of generated water catalyzed by Amberlyst-15.[4b] But, unfortunately, these acidic resins had low thermal stability due to their organic frameworks and were normally used below 130 °C, which partially limited their applications. Very recently, as high as 91.2% HMF yield was obtained by using a carbon-based catalyst in our group and this material also showed good stability and reusability.[6] However, the most important industrial method for fructose production is by the enzymatic isomerization of glucose syrup, a process yielding only about 50% fructose.[7,8] So if glucose or glucose-based carbohydrate was directly used as the raw reactant, the industrial process for the production of HMF would be much more economical and beneficial.



**Scheme 1** Schematic representation of the glucose isomerization to fructose using enzyme, Lewis acid or base catalysts and the fructose dehydration to HMF with acid catalysts.

The challenge of using glucose as a raw material is the stability of the glucose ring, which makes the dehydration processing much more difficult. It has been reported that the conversion of glucose into HMF could proceed in two steps: the first isomerization of glucose to fructose in the presence of enzyme, Lewis acid or base catalysts (Scheme 1),[9–12] followed by the dehydration of fructose to HMF. Enzymatic process is highly selective, but it has several disadvantages including the use of buffering solutions to maintain pH, narrow operating temperatures, strict feed purification requirements, and periodic replacement of the enzyme due to irreversible deactivation.[8,12a,13] On the other hand, combination of solid acid and base in a single high-boiling-point solvent, realizing the goal of glucose dehydration to HMF,[10,11] would make this process much more

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complicated and greatly increase the cost of the separation of HMF from the solvent.[3,14]

The common Lewis acid, $CrCl_2/CrCl_3$ or $SnCl_4$ has shown good activity for the conversion of glucose into HMF in ionic liquid solvent and the yield of HMF was in the range of 60% to 70%.[15a,b] But the chromium ion is toxic and the process for the recycling of $SnCl_4$ is still a problem. Alternatively, a heterogeneous catalyst containing $Sn^{4+}$ ions would be a good choice to convert glucose-based carbohydrates to HMF. Davis *et al.* found that Sn-beta could efficiently catalyze the isomerization of glucose to fructose and then convert the generated fructose to HMF rapidly with hydrochloric acid at low pH.[8,15c] $Sn^{4+}$ ions as Lewis acids were active for the glucose isomerization to fructose and the partially hydrolyzed Sn–OH groups were acted as Brønsted acid for the generated fructose dehydration, and this analysis was also in accordance with Corma's reports in the MPV reaction.[16,17] Recent NMR studies have showed that Sn-beta isomerizes glucose to fructose *via* 1,2-intra-hydride transfer with an intermediate of 3-deoxy-glucosone.[12b] However, for the synthesis of Sn-beta, a certain amount of hydrofluoric acid (HF) must be used.[8,14,15c] HF is highly corrosive, noxious, easy to volatilize and is very harmful to humans and the environment, and so makes this synthetic process less eco-friendly. Besides, single Sn-beta catalyst was only active for the isomerization of glucose to fructose and an external acid catalyst, such as HCl or Amberlyst-15, should be added to the reaction system to convert the generated fructose to HMF.

In recent years, an abundant and cheap clay material exchanged with $Sn^{4+}$ ions was widely used in many organic reactions, such as cyanosilylation of carbonyl compounds, ring-opening polymerization of lactones, Baeyer–Villiger oxidation reaction, and much satisfied results was obtained.[18,19] However, there were almost no reports about tin-ion-exchanged clay used in the dehydration of carbohydrates. Herein, an Sn-Mont catalyst, which was easily prepared *via* the ion-exchange of natural calcium montmorillonite (Ca-Mont) with an aqueous tin tetrachloride solution, was used to investigate its activity in the conversion of glucose, disaccharides, even polysaccharides to HMF.

## 2. Experimental

### 2.1 Materials

5-Hydroxymethylfurfural (99.5%) and levulinic acid were purchased from Alfa Aesar Chemical Reagent Company. Amberlyst-15, inulin and cellulose were purchased from Aladdin Reagent Limited Company. Calcium montmorillonite (Ca-Mont) was purchased from Zhejiang San-Ding Technological Reagent Limited Company (China). $SnCl_4{\cdot}5H_2O$, $SnO_2$, NaCl, fructose, glucose, sucrose, cellobiose and starch was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Tetrahydrofuran (THF), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide (DMA), *N*-methyl pyrrolidone (NMP) were chemical pure solvents and purchased from shanghai chemicals company.

### 2.2 Catalyst preparation

In a typical synthesis, Ca-Mont was ion-exchanged with an aqueous solution of $SnCl_4{\cdot}5H_2O$ at 50 °C for 24 h. The collected clay was washed with water until the washing water was neutral (pH = 7). Finally, Sn-Mont was dried at 100 °C overnight, followed by being ground to powder in a mortar with a pestle and stored in a glass bottle.

### 2.3 Characterizations of the catalyst

**XRD, EDX, SEM and BET characterization.** X-ray powder diffraction (XRD) patterns were recorded on a Bruker diffractometer with Cu Kα radiation ($\lambda$ = 1.5406 Å). The energy dispersive X-ray analysis (EDX) was employed for the quantitative elemental analysis and measured on a Hitachi S-3400N SEM coupled parallel to an energy dispersive X-ray spectrophotometer (Bruker Quantax 200). The nitrogen adsorption experiment was measured at 77 K on a NOVA 4200e sorption analyzer. Before measurements, the samples were outgassed at 200 °C for 6 h.

**Pyridine-adsorbed FT-IR characterization.** The IR spectrum of the pyridine-adsorbed Sn-Mont was obtained in the transmission mode using a Nicolet Model 710 spectrometer. Firstly, the catalyst (50 mg) was grounded into fine powders and pressed into a very thin self-supporting wafer. The disc was mounted in a quartz IR cell equipped with a $CaF_2$ window and a vacuum system. Prior to adsorption, the sample disc was pretreated *in situ* at 200 °C for about 2 h under evacuation, then cooled to room temperature when pyridine vapor was introduced into the cell for 0.5 h. The physically adsorbed pyridine was removed by evacuating for 1 h and a spectrum was subsequently recorded.

**$NH_3$-TPD characterization.** Temperature-programmed desorption of ammonia ($NH_3$-TPD) was performed on an apparatus PX200 (Tianjin Golden Eagle Technology Limited Corporation). The sample (50 mg) was pretreated at 200 °C for 2 h and then cooled to room temperature under a $N_2$ flow. Pure $NH_3$ was injected until adsorption saturation was reached, followed by a flow of $N_2$ for 1 h. Then the temperature was raised from 90 to 500 °C with a heating rate of 10 °C $min^{-1}$ and the amount of desorbed ammonia was detected by using thermal conductivity detector (TCD) at 110 °C. Besides, a blank measurement was conducted without adsorption of ammonia and after deducted the blank measurement, the $NH_3$-TPD curve of Sn-Mont was obtained.

### 2.4 Dehydration of carbohydrates to HMF

The reactions were performed in a stainless steel autoclave (50 mL) heated in a temperature-controlled oil bath. The mixture of carbohydrates, solvent (monophase: 4.2 mL THF with 1.8 mL DMSO; biphase: 5 mL organic phase with 1 mL $H_2O$) and catalyst (0.2 g) were put in the sealed autoclave equipped with a magnetic stirring bar. $N_2$ gas was used for purging air inside the reactor and keeping a certain pressure to prevent boiling. After reaction, the reactor was cooled to room temperature by loading cooling water. The solid catalyst was removed by filtration, and the filtrate was taken for analysis. The recovered Sn-Mont catalyst was washed with water and ethanol, then dried at 100 °C for the next run.

### 2.5 Product analysis

The analysis of the reaction products were carried out by means of an HPLC apparatus (Agilent 1200 Series) equipped with an XDB-C18 column (Eclipse USA) operated at 35 °C based on the external standard. An auto-sampler (Agilent G1329A) was used to enhance the reproducibility. HMF was quantified with an ultraviolet detector (Agilent G1314B) at 282 nm. The eluent with flow rate of 0.6 mL $\text{min}^{-1}$ was a mixture of methanol to water volumetric ratio of 20 : 80. The carbohydrates concentration was analyzed with a refractive index detector (Agilent G1362A). The eluent was pure water with a flow rate of 1.0 mL $\text{min}^{-1}$. Conversion of glucose or fructose and yield of HMF were defined as follows:

$$\text{Glucose or fructose conversion} = \text{moles of glucose or fructose reacted}/\text{moles of starting glucose or fructose}$$

$$\text{HMF yield} = \text{moles of HMF produced}/\text{moles of starting glucose or fructose}$$

For disaccharides and polysaccharides, HMF yields were defined as follows:

$$\text{HMF yield} = \text{moles of HMF produced}/\text{moles of hexose units in poly} - \text{saccharides}$$

## 3. Results and discussion

### 3.1 Characterization of catalyst

**XRD, EDX, SEM and BET analysis.** The X-ray powder diffraction (XRD) patterns (not shown) confirmed that the structure of montmorillonite was maintained and no peaks of tin compounds appeared, which means the ion-exchanging process had no influence on the structure of then montmorillonite material. Furthermore, the EDX analysis showed that no calcium atoms were detected in the final Sn-Mont material, indicating that all of the calcium ions were fully exchanged. The SEM image showed that the prepared sample did not display well shaped crystalline particles and the BET surface area was 149.1 $m^2\ g^{-1}$.

**$NH_3$-TPD analysis.** The temperature programmed desorption of ammonia was measured to characterise the acidity of the Sn-Mont catalyst (Fig. 1). There are two desorption peaks, the low temperature desorption peak indicated weak adsorption acidic sites, and the peak at high temperature is attributed to the interaction of $NH_3$ with moderate acid sites.

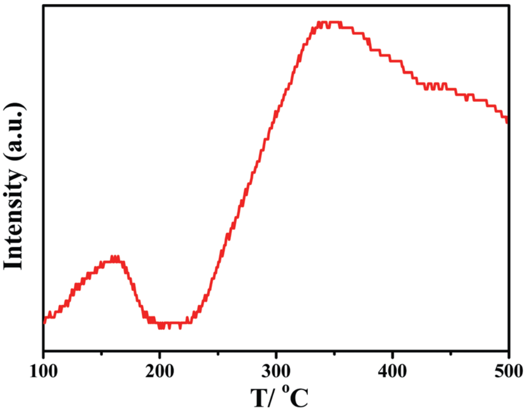

**Fig. 1** $NH_3$-TPD profile of the Sn-Mont catalyst.

**Pyridine-adsorbed FT-IR analysis.** The type of acid on Sn-Mont catalyst was determined by pyridine adsorption infrared spectroscopy and the spectrum in 1390–1580 $\text{cm}^{-1}$ range is shown in Fig. 2. There are three bands in this region. The one at about 1444 $\text{cm}^{-1}$, arising from the C–C stretching vibration of a coordinatively bonded pyridine complex, indicated the presence of Lewis acid sites. The one at 1540 $\text{cm}^{-1}$ is attributed to the C–C stretching vibration of pyridium ion and has been used for the identification of the Brønsted acid sites. Another peak at about 1490 $\text{cm}^{-1}$ was characteristic of pyridine adsorbed on both Lewis and Brønsted acid sites.[19a] The results showed that Sn-Mont exhibited both Brønsted acidity and Lewis acidity.

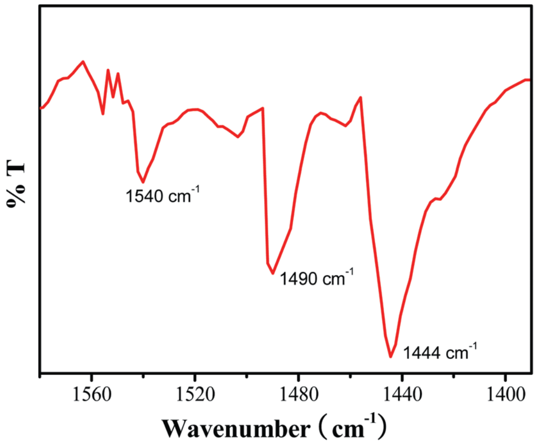

**Fig. 2** Pyridine-adsorbed FT-IR spectra (pure power pressed discs) on Sn-Mont catalyst.

### 3.2 Determination of the suitable conditions for glucose conversion in mixed organic solvent

**Effect of solvent.** The activity of Sn-Mont for the glucose conversion in various solvents was investigated and the results are presented in Fig. 3. From the results, we can see that the Sn-Mont catalyst exhibited low activity in water, with the glucose conversion of 40.2% and HMF yield of 6.5% at 160 °C for 3 h. This is because water is not favorable for the dehydration reaction and can promote the rehydration of HMF to by-products, such as levulinic acid. Except water, good HMF yields were obtained in organic solvents, such as in DMF, DMA, NMP and DMSO. Especially in DMSO, the higher yield of HMF (43.6%) was obtained because in which the furanoid form is preferred and the side reactions are remarkably suppressed.[6,20] However, these solvents have high boiling-points (>150 °C) and much energy should be inputted to separate HMF from the reaction medium. On the other hand, a poor yield of HMF was obtained from low the boiling-point solvent as well, due to the poor solubility of glucose in pure THF. To solve this problem,

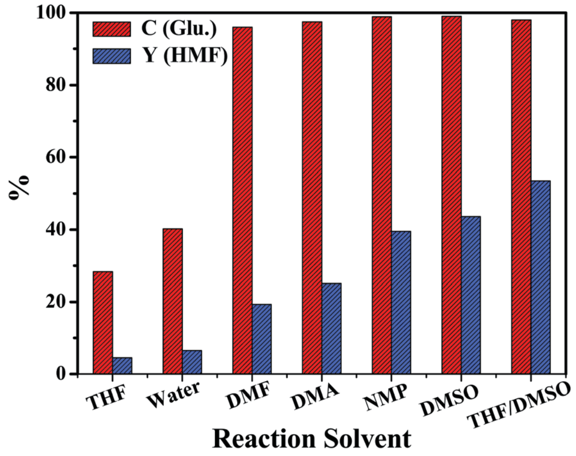

**Fig. 3** Glucose conversion and HMF yield in diverse solvents by Sn-Mont catalyst. (*Reaction conditions*: 6 mL reaction mixture, 5 wt% glucose, 0.2 g Sn-Mont catalyst, 160 °C, 3 h.)

we tried to use a THF–DMSO mixed organic solvent system and found the yield of HMF was increased with the increase of THF percentage in DMSO. At the volume ratio of 70 : 30, the yield of HMF reached 53.5% at 160 °C for 3 h, so this novel Sn-Mont catalyst was very efficient to directly catalyze glucose dehydration to HMF in this THF–DMSO system without adding any other Brønsted acid. Further increase the percentage of THF, the solubility of glucose decreases rapidly. Therefore, a THF–DMSO mixture of 70 : 30 (v/v) was employed as reaction media hereafter.

**Effect of reaction temperature with reaction time.** Subsequently, the influence of reaction temperature on HMF yield and glucose conversion was investigated and the results are shown in Fig. 4. At lower temperatures (100 °C and 120 °C), the yield of HMF was very low and the conversion of glucose was below 60%. Further increasing the reaction temperature to 140 °C, the activity of the Sn-Mont catalyst increased rapidly and a higher HMF yield and glucose conversion were obtained. As high as 53.5% yield of HMF was gained with 98.4% glucose conversion at 160 °C for 3 h. In this study, reaction at higher temperatures was not applied since higher temperatures will cause high energy-consumption and difficulties in control. Therefore, the reaction temperature of 160 °C was employed as the reaction conditions hereafter.

**Effect of glucose concentration.** Generally, the substrate concentration has a significant influence on the HMF yield for heterogeneous catalytic reactions. Thus the effect of initial glucose concentrations including 5 wt%, 7wt% and 10 wt% on the dehydration of glucose to HMF was investigated (Table 1, entries 1, 2 and 3). It can be seen that the glucose conversion and HMF yield were partly affected by the initial concentration of glucose. The highest HMF yield was 53.5% at 5 wt% of initial glucose concentration. In addition, when the glucose concentration was increased to 10 wt%, the yield of HMF was still high (42.4%), indicating the high efficiency of Sn-Mont catalyst. The partial loss of HMF at high glucose concentration might be attributed to the higher glucose concentration leading to higher rates of side-reactions with the production of some undesired by-products.[3,21]

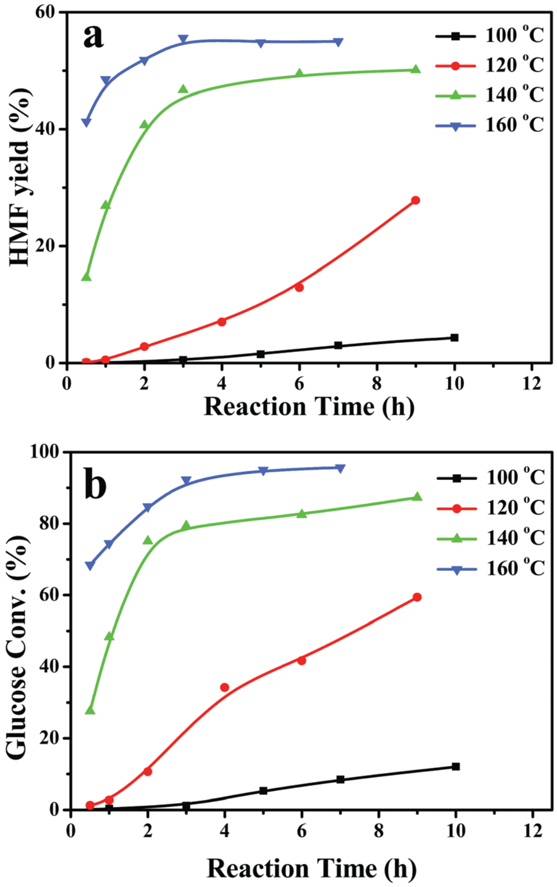

**Fig. 4** Influence of the reaction temperature on HMF yield (a) and glucose conversion (b). (*Reaction conditions*: 6 mL of reaction solution, THF–DMSO = 70 : 30 v/v, 5 wt% glucose, 0.2 g Sn-Mont catalyst.)

**Table 1** Summary of the glucose conversion and HMF yield catalyzed by various heterogeneous catalysts[a]

| Entry | Catalyst | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | Sn-Mont | 98.4 | 53.5 |
| 2[b] | Sn-Mont | 98.6 | 48.2 |
| 3[c] | Sn-Mont | 98.7 | 42.4 |
| 4[d] | Sn-Mont | >99% | 78.1 |
| 5 | Amberlyst-15 | 78.7 | 7.0 |
| 6 | Ca-Mont | 48.0 | 0 |
| 7 | No catalyst | 5.2 | 0 |
| 8 | $SnO_2$ | 25.0 | 0 |
| 9 | $SnCl_4\cdot5H_2O$ | 31.4 | 0 |
| 10 | Sn-Mont[e] | 65.7 | 8.3 |

[a] *Reaction conditions*: 10 mL of reaction solution, THF–DMSO = 70 : 30 (v/v), 160 °C, 3 h. [b,c] The initial concentration of glucose was 7 wt% and 10 wt%, respectively, and other default initial concentration was 5 wt%. [d] Fructose was used as the reactant for 1 h. [e] Sn-Mont was calcined at 600 °C for 4 h.

**Effect of the dose of Sn-Mont catalyst.** Although the mass ratio of Sn-Mont catalyst to glucose is 2 : 3 (m/m), the reaction can proceed at lower catalyst loading and the results were shown

**Table 2** Glucose conversion and HMF yield with Sn-Mont as the catalyst[a]

| Entry | Sn-Mont (g) | Conversion (%) | Yield (%) |
|---|---|---|---|
| 1 | 0.4 | 98.2 | 33.3 |
| 2 | 0.2 | 98 | 53.5 |
| 3 | 0.1 | 91.2 | 48.5 |
| 4 | 0.04 | 89.9 | 44.6 |
| 5 | 0.02 | 89.5 | 39.8 |

[a] *Reaction conditions*: 5 wt% glucose, 160 °C, 3 h, 6 mL of reaction solution, THF–DMSO = 70 : 30, v/v.

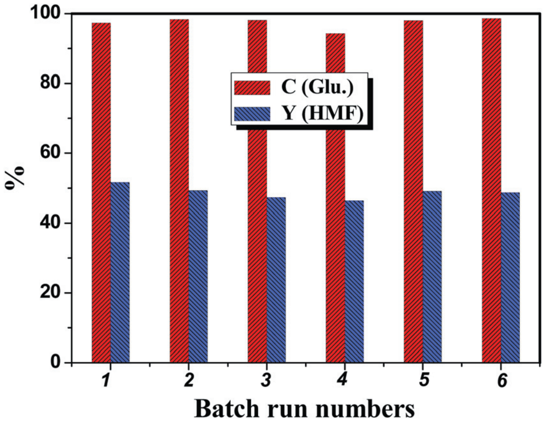

**Fig. 5** Glucose conversions and HMF yields of Sn-Mont in cycle usage test. (*Reaction conditions*: 0.2 g Sn-Mont, 5 wt% glucose, 6 mL of reaction solution, THF–DMSO = 70 : 30, v/v. 160 °C, 3 h.)

in Table 2. As the catalyst amount is decreased to 0.02 g, glucose conversion and HMF yield were still high, about 89.5% and 39.8%, respectively. With the aim to obtain high yields of HMF, the ratio of catalyst to glucose of 2 : 3 (m/m) was chosen hereafter.

### 3.3 Catalyst recyclability

The recyclability is of great importance for applying a catalyst in industrial processes. The recyclability of the Sn-Mont catalyst was evaluated through six repeated reactions. The results in Fig. 5 indicated that the Sn-Mont catalyst exhibited excellent stability for glucose conversion into HMF. After being used six times at 160 °C for 3 h, the glucose conversions and HMF yields were always about 98% and 53%, respectively. The SEM and $N_2$ sorption showed that the morphology of the used Sn-Mont did not change and the BET surface area of it remained about 149 $m^2\ g^{-1}$. Moreover, the $NH_3$-TPD profile of the used Sn-Mont was similar to that of the fresh one. Therefore, it can be concluded that the catalyst was stable in this system, at least being used six times.

### 3.4 Comparison of catalyst activity and effect of Sn-Mont catalyst on reaction pathways

Generally, the conversion of glucose to HMF would undergo two successive steps: isomerization to fructose by Lewis acid and then the generated fructose being dehydrated to HMF by Brønsted acid. Tin ions used as Lewis acid sites to isomerize aldose (xylose or glucose) to ketose (xylulose and fructose, respectively) has been widely reported.[8,14,15*c*,22] When Amberlyst-15, a typically strong Brønsted acid catalyst was used, a poor HMF yield of 7% with 78.5% glucose conversion at 160 °C for 3 h was obtained (Table 1, entry 5). This indicated that this novel Sn-Mont catalyst containing both types of acidic sites led to the direct conversion of glucose to HMF in a one-pot process. Besides, no significant amount of fructose was detected in the reaction solution and the conversion of fructose was nearly up to 100% with 78.1% HMF yield at 160 °C in 1 h if fructose was used as the reactant (Table 1, entry 4), which meant that the dehydration of fructose to HMF is very fast and the Brønsted acid on the Sn-Mont was active enough for the generated fructose to be rapidly dehydrated to HMF.

The pyridine-adsorbed FT-IR spectrum confirmed the existence of two types of acid sites on the Sn-Mont catalyst, which was also in accordance with the experimental results. However, the pristine Ca-Mont catalyst, with two types of acid sites as well, only resulted in the formation of certain amounts of undetermined by-products without HMF formation (Table 1, entry 6), which indicated that tin ions were the main Lewis active sites to catalyze the glucose isomerization to fructose. In blank solution (without adding any catalyst), no HMF was detected, indicating the auto-catalysis was negligible (Table 1, entry 7). Davis *et al.* reported that the active sites for the isomerization reaction were $Sn^{4+}$ ions exchanged into the framework of the beta zeolites.[8,12*a*] In our experiments, we also found a similar phenomenon that either $SnO_2$ or $SnCl_4{\cdot}5H_2O$ showed low isomerization activity and the conversion of glucose was below 32% (Table 1, entries 8 and 9). After being exchanged with montmorillonite, the glucose conversion was almost complete. However, after calcination at 600 °C for 4 h to condense Sn–OH groups, Sn-Mont showed much lower activity for glucose conversion, only 8.3% yield of HMF was obtained with 65.7% glucose conversion (Table 1, entry 10), which meant that Sn–OH were the Brønsted acid sites to catalyze the generated fructose dehydration to HMF as schemed on Fig. 6.

### 3.5 Conversion of di/poly-saccharides on Sn-Mont catalyst

The robustness of Sn-Mont catalyst in synthesizing HMF from glucose opens up the possibility of using more complex carbohydrates, such as disaccharides (sucrose and cellobiose) and polysaccharides (inulin, starch and cellulose) as renewable raw material. Synthesis of HMF from cellobiose, inulin, starch, and cellulose, involves the hydrolysis, isomerization and dehydration steps with an acid or enzyme and makes the process very complicated.[2,23–26] Here, sucrose, cellobiose and inulin could be converted into HMF with our catalyst and the yield of HMF was above 40% without coupling with other acid or enzyme catalysts (Fig. 7). However, the HMF yield from starch and cellulose was quite poor under the same conditions. This is because the hydrolysis of starch/cellulose to glucose is difficult in the organic phase, affording a HMF yield below 2%.

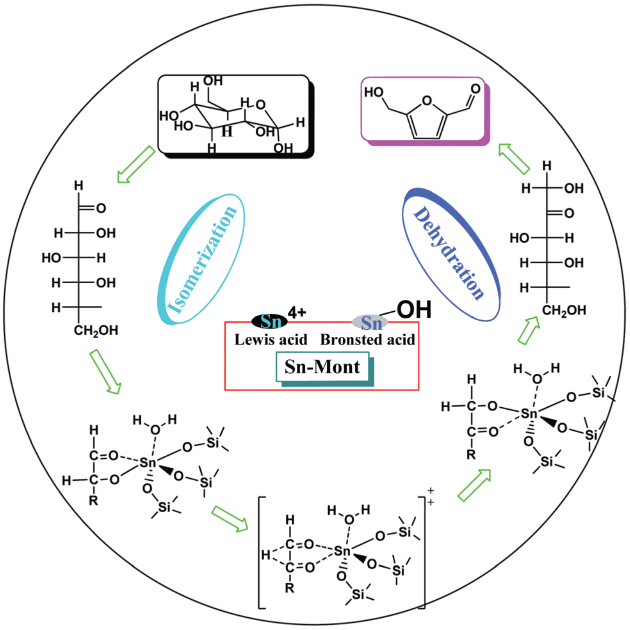

**Fig. 6** Plausible reaction mechanism for glucose isomerisation to fructose following dehydration to HMF on Sn-Mont catalyst.

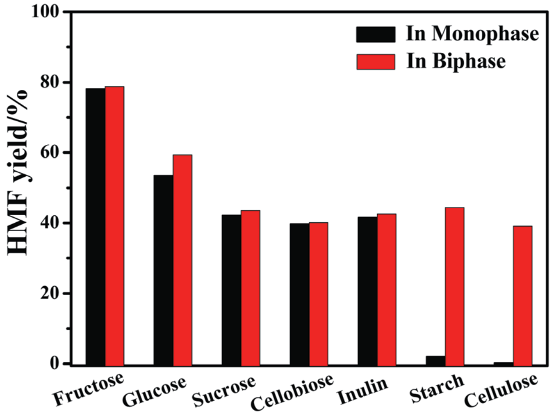

**Fig. 7** HMF yields from various carbohydrates in THF/DMSO monophase (a) and biphase THF/$H_2O$–NaCl solvent with adding NaCl (b). (*Reaction conditions*: (a) 0.2 g Sn-Mont, 5 wt% carbohydrates, 6 mL of reaction solution, THF–DMSO = 70 : 30, v/v, 160 °C, 3 h; (b) 0.2 g Sn-Mont, 5 wt% carbohydrates, 6 mL of reaction solution, 0.37 g NaCl, 1 mL $H_2O$, 5 mL THF, 160 °C, 3 h.)

### 3.6 Catalyst activity in biphasic solvent for carbohydrates conversion

In order to further lower the boiling point of the reaction system and make the separation of HMF easy and effective, water was utilized to replace DMSO to generate a biphasic reaction system for glucose conversion. After reaction at 160 °C for 3 h, the HMF concentration in the organic phase (0.01675 g $mL^{-1}$) was 4.4 times higher than that in aqueous phase (0.00381 g $mL^{-1}$), and the total HMF yield was about 41.7%, a little lower than in the monophase solvent, due to partial HMF dehydration to levulinic acid in the aqueous phase which is catalyzed by Sn-Mont.

To enhance the HMF yield, NaCl was added to solvents as indicated in the previous report.[27] As expected, we found that almost all of HMF was transferred into the organic phase (0.0249.1 g $mL^{-1}$, almost no HMF in aqueous phase) and the HMF yield increased to 59.3%, higher than obtained in the monophase as well, which indicated that the addition of NaCl not only increased the partitioning coefficient between THF and water, but also inhibited the generated HMF from further dehydration to levulinic acid. Moreover, the THF/$H_2O$–NaCl system was also effective to convert fructose and di-/poly-saccharides. HMF yields from fructose, sucrose, cellobiose and inulin were 78.8%, 43.6%, 40.1% and 42.6%, respectively (Fig. 7). These values are a little higher than that obtained in single phase systems, indicating that this biphase system could inhibit the side reactions. The stability of the Sn-Mont catalyst in this THF/$H_2O$–NaCl biphasic system was also confirmed. After being used 4 times at 160 °C for 3 h, the yield of HMF was always about 58%. The leaching of tin in the aqueous phase was negligible (<0.005% detected by ICP-AES), which was also proved the stability of the GTS catalyst. More importantly, HMF yields obtained from starch and cellulose were greatly exceeded in the monophase system without the addition of other mineral acids and the yields reached 44.4% and 39.1%, respectively. These results are very promising since they show that Sn-Mont can be used directly for the conversion of complex carbohydrates to HMF without coupling with other acid catalysts.

## 4. Conclusions

In summary, a Sn-Mont catalyst was synthesized easily *via* an eco-friendly ion-exchanged method. This Sn-Mont catalyst was used for the direct conversion of glucose or glucose-based carbohydrates into HMF and displayed high activity and good stability. For glucose, the yield of HMF can mount to 53.5% in THF–DMSO mixed solvent and 59.3% in the biphase. Especially, for raw biomass starch and cellulose, the HMF yields can reach 44.4% and 39.1%, respectively, in THF/$H_2O$–NaCl biphasic system. It is confirmed that the key to successfully achieving the direct conversion of the glucose-unit carbohydrate to HMF is that Sn-Mont contains both Brønsted acid and Lewis acid sites and combines the isomerization process with the dehydration step in an one-pot reaction system without the addition of any other acid catalysts. Hence, the approach we described with the Sn-Mont catalyst in mono-/biphase system, due to its green preparation, high activity, and high reusability, has excellent potential for the conversion of biomass into biofuels and platform chemicals.

## Acknowledgements

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