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One-pot conversion of carbohydrates into 5-ethoxymethylfurfural and ethyl D-glucopyranoside in ethanol catalyzed by a silica supported sulfonic acid catalyst

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In this study, prepared silica supported sulfonic acid was used as a heterogeneous catalyst for the production of 5-ethoxymethylfurfural (EMF) from fructose based carbohydrates and the synthesis of ethyl D-glucopyranoside from glucose based carbohydrates in ethanol. EMF was obtained in a high yield of 83.8% from 5-hydroxymethylfurfural (HMF) after 10 h, and a 63.1% yield was obtained from fructose at 100 °C for 24 h. Temperature experiments demonstrated that a higher reaction temperature (in the case of 120 °C) resulted in side reactions such as polymerization of HMF and alcoholysis of HMF into ethyl levulinates. When di- and poly-saccharides (sucrose and inulin) were used, the fructose moieties in sucrose and inulin were also successfully converted into EMF. However, the silica supported sulfonic acid catalyst was inert for the production of EMF from aldose based carbohydrates such as glucose and cellobiose. Ethyl D-glucopyranoside was formed in a high yield of 91.7% from glucose. More importantly, the catalyst could be reused several times without losing its catalytic activity with an average EMF yield of around 60% from a one-pot reaction of fructose. This work provides a good outlook for the conversion of carbohydrates into fine chemicals and biofuel additive.

Introduction

With the development of the global economy, fossil resources are expected to shrink significantly in the next few decades. Therefore, in the near future, the world will need to gradually develop renewable resources to replace the use of fossil resources for energy consumption and platform chemicals.[1–3] Renewable biomass with an estimated annual production of 1.0×10^{11} tons per year is considered to be a promising alternative to fossil resources to supply sustainable raw material for the production of biofuels and chemicals.[4–6] In the past decades, much effect has been devoted to the development of efficient catalytic routes for the production of biofuels and bio-chemicals from biomass resources.[7] Among the bio-based chemicals, 5-hydroxymethylfurfural (HMF) is recognized as one of the top building-block chemicals according to the ''Top Value Added Chemicals'' proposed by the US Department of Energy.[8] It can be used as a valuable intermediate for the production of fine chemicals, pharmaceuticals and furan-based polymers.[9] In addition, drop-in biofuel candidates such as 5-ethoxymethylfurfural (EMF) and 2,5-dimethylfuran (DMF) can also be obtained by the treatment of HMF.[10–12] In the past decades, considerable work has been devoted to the production of HMF in various systems including water, organic solvents, ionic liquids (ILs) and using a biphasic system. Moderate to high HMF yields were obtained from fructose and glucose, even directly from cellulose and lignocelluloses.[13–16]

Recently, EMF derived from HMF is considered to be one of the promising next-generation biofuels. It has a high energy density of 8.7 kWh L^{-1}, which is comparable with those of standard gasoline (8.8 kWh L^{-1}) and diesel fuel (9.7 kWh L^{-1}), and significantly higher than the widely familiar bio-ethanol (6.1 kWh L^{-1}).[17] Surprisingly, the synthesis of EMF from carbohydrates has remained largely unexplored, despite its good prospect as a biofuel. One of the quantitative conversion methods for the synthesis of EMF was *via* the treatment of 5-chloromethylfurfural (CMF) with ethanol.[18] The intermediate CMF was produced by the treatment of carbohydrates in a solution of lithium chloride (5 wt.%) in concentrated hydrochloric acid, and it was extracted by 1,2-dichloroethane. Alternatively, the synthesis of EMF has also been reported by the direct etherification of HMF with ethanol in the presence of acid catalysts.[19,20] Although a high EMF yield was achieved from HMF or CMF, it was desirable to carry out the research

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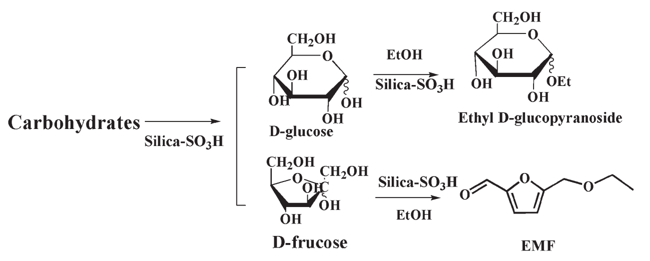
for the synthesis of EMF directly from carbohydrates without the separation of the intermediate such as HMF, which saves time and energy. Fructose is regarded as a preferable feedstock for the production of HMF with a high conversion and a high selectively. Recently, some methods were developed for the synthesis of EMF from fructose, which combines the dehydration of fructose into HMF followed by the etherification of HMF to EMF. Recently, 5-alkoxymethylfurfural ethers have been synthesized directly from fructose using ionic liquids (imidazolium propanesulfonic acids) as catalysts with an approximate yield of 55%.[21] Yang *et al.* reported that EMF could be synthesized from fructose in a yield of 65% catalyzed by the heteropolyacid $H_3PW_{12}O_{40}$ under microwave heating.[22] However, $H_3PW_{12}O_{40}$ was soluble in ethanol and so recycling of the catalyst was difficult. Although the authors carried out the recycling experiments, the procedure seemed tedious. The catalyst was recovered by the distillation of solvents and products under vacuum. In our group, we have also developed a new method for the synthesis of fructose into EMF in a high yield catalyzed by an organic–inorganic hybrid solid catalyst, $[MIMBS]_3PW_{12}O_{40}$.[23] Due to the high hygroscopicity of this material, caution is needed with regards to the storage and utilization of $[MIMBS]_3PW_{12}O_{40}$. Therefore, there is still a high demand to develop new green chemistry catalytic routes for the synthesis of EMF from carbohydrates.

Grafting soluble acids on the surface of an inorganic insoluble support is a strategy to transform high-performance soluble acids into heterogeneous solid catalysts, which have advantages of a strong acid site, large surface area, and they are easily separated and recycled.[24,25] Over the last decades, sulfonic acid ($-SO_3H$) was usually chosen as a functional group, because it is not only known for its efficient proton acid catalytic ability, but it can also be easily incorporated into many different materials.[26,27]

Herein, in continuation with our investigation on the development of a new catalytic system and the expansion in the utilization of carbohydrate substrates, propyl sulfonic groups were immobilized on mesoporous silica to construct silica supported sulfonic acid as a heterogeneous catalyst, and its catalytic activity was studied for the synthesis of EMF from carbohydrates (Scheme 1). This catalyst was found to be effective for the conversion of fructose unit based carbohydrates into HMF and it also demonstrated a good activity for the direct etherification of glucose into ethyl D-glucopyranoside. Although ethyl D-glucopyranoside is not a liquid fuel, it been widely used as a biodegradable surfactant and a chemical intermediate.[28] This method generates a sustainable strategy for the conversion of biomass into biofuels and chemicals.



Scheme 1 Illustration for the synthesis of EMF and ethyl D-glucopyranoside from carbohydrates in ethanol.

Experimental section

Materials and methods

3-Mercaptopropyltrimethoxysilane (99.8%) was purchased from Aladdin Chemical Reagent Co., (Shanghai, China). 35 wt.% H_2O_2 was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Ethanol (99.5%), *n*-hexadecylamine and tetraethoxysilane (TEOS, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China), and ethanol (99.5%) was freshly distilled before use. 5-Hydroxymethylfurfural (98%) was supplied by Beijing Chemicals Co. Ltd. (Beijing, China). 5-Ethoxymethylfurfura (98%) was purchased from Hangzhou Imaginechem Co., Ltd. (Zhejiang, China). Ethyl D-glucopyranoside was purchased from Feiyang Biotechnology Co. Ltd. (Shangdong, China). Sucrose, inulin and cellobiose were purchased from J & K Co. Ltd. (Beijing, China). Fructose was puchased from Sanland-Chem International Inc. (Xiamen, China). Glucose was purchased from ABCR GmbH & Co. (Karlsruhe, Germany). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). All other reagents were provided by local supplies (Wuhan, China) without further purification.

Preparation of the catalyst

Silica sulfate was prepared according to a known procedure.[29,30] Typically, 3.2 g (0.013mol) of *n*-hexadecylamine was dissolved in 100 mL mixed solution of ethanol and water (the volume ratio of ethanol to water: 21 : 27) at room temperature. Then 8.3 g of tetraethoxysilane (TEOS, 0.039 mol) and 1.97 g of 3-mercaptopropyltrimethoxysilane (MPTMS, 0.01 mol) were added to the above mixture in sequence. The resulting solution was stirred for 24 h at room temperature and the slurry was filtered to obtain a white solid. *n*-Hexadecylamine was removed through soxhlet extraction by ethanol at reflux temperature for 24 h to give rise to propyl thiol modified mesoporous silica. Then, thiol groups were oxidized by 35% aqueous H_2O_2 (2 g g^{-1} of solid) at room temperature for 24 h in a methanol/water mixture. After reaction, the white solid was washed with ethanol and water, and then the resulting solid was stirred for 4 h in 0.1 M H_2SO_4 (1 g of solid per 100 mL of solution). Finally, the prepared silica supported propyl sulfonic acid (Silica-SO_3H) catalyst was filtered and washed extensively with deionized water until the filtrate was neutral. The recovered Silica-SO_3H was dried in an oven at 100 °C in vacuum over night.

Catalyst characterization

Fourier transform infrared (FT-IR) measurements were recorded on a Nicolet NEXUS-6700 FTIR spectrometer with a spectral resolution of 4 cm^{-1} in the wave number range of 500–4000 cm^{-1}. N_2 absorption–desorption experiments were carried out at −193 °C using a Quantachrome Autosorb-1-C-

MS instrument. Silica-SO_3H was subjected to outgassing for 6 h at 200 °C before the experiment. The surface area was obtained by using the BET method. The pore size distribution was evaluated from the desorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. The content of sulfur and carbon was conducted on a 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer).

Titration of solid

0.1 g of the solid catalyst was added to 10 mL of aqueous KCl (0.1 M) and stirred for 30 min. The resulting solution was titrated by a standard solution of KOH (0.02 M) and the pH evolution was determined by a Metrohm pH meter.

Synthesis of EMF from the etherification of HMF

Firstly, HMF (126 mg, 1 mmol), ethanol (5 mL) and Silica-SO_3H catalyst (200 mg) were added into a 10 mL round bottom flask with a condenser, which was sealed with a balloon. Then, the reaction mixture was carried out at a set temperature for the desired reaction time under an atmospheric pressure with a magnetic stirrer. Samples were withdrawn, diluted with water, centrifuged at 12 000 rpm for 5 min, and analyzed by an HPLC system.[31]

Synthesis of EMF from fructose or ethyl D-glucopyranoside through a one-pot reaction

D-Fructose (180 mg, 1 mmol) or glucose (180 mg, 1 mmol) was firstly dissolved in ethanol (5 mL) at a set temperature. Then the Silica-SO_3H catalyst (200 mg) was added into the reaction system, and the reaction was carried out at a set temperature. Otherwise the procedure followed in a manner similar to that discussed above.

Determination of the products

HPLC analysis of HMF and EMF were done on VARIAN ProStar 210 HPLC system coupled with a UV detector. Samples were separated by a reversed-phase C18 column (200 × 4.6 mm). The column temperature was maintained at 25 °C. The optimized mobile phase consisted of acetonitrile and 0.1 wt.% acetic acid aqueous solution with the volume ratio at 15 : 85. The flow rate was set at 1.0 mL min^{-1}. The detection wavelength was 280 nm. The content of HMF and EMF in samples were obtained directly by interpolation from calibration curves, with a coefficient of 0.999.

Ethyl D-glucopyranoside was separated with an aminex HPX-87 column (Agilent) and Waters 2412 Refractive Index detector.

Recycling of the catalyst

At the end of the reaction, the Silica-SO_3H catalyst was recovered by filtration. The recovered catalyst was washed three times with 10 mL of water, three times with 10 mL of ethanol, three times with 10 mL of diethyl ether, and then it was dried at 80 °C over night in a vacuum oven.

Results and discussion

Catalyst characterization

The IR spectra of the Silica-SO_3H catalyst is shown in Fig. 1. The absorption at 3447 cm^{-1} was attributed to the hydroxyl groups. The band near 1088 cm^{-1} was assigned to the asymmetric stretching modes of Si–O–Si bond, indicating the structure of support silica.[32] Three bands appeared at 1200–1250, 1010–1100 and 685 cm^{-1}, which were attributed to the O=S=O asymmetric and symmetric stretching vibration and S–O stretching vibration of the sulfonic groups (–SO_3H), respectively.[32] The band presented at 805 cm^{-1} was assigned to the C–S stretching vibration. In addition, the bands at 2927 cm^{-1} and 612 cm^{-1} were attributed to the stretching vibration and the bending vibration of the C–H bond in the propyl sulfonic acid group, respectively. These results clearly indicated that the propyl sulfonic acid group was successfully grafted onto the surface of the silica support.

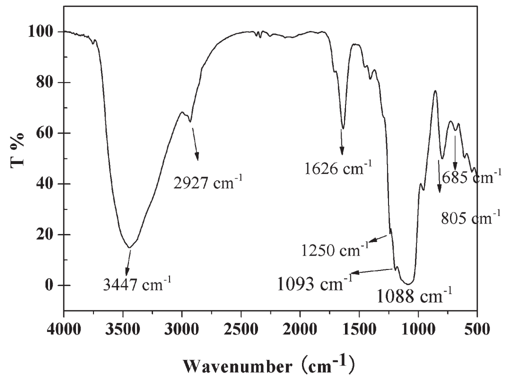


Fig. 1 FTIR spectrum of the Silica-SO_3H catalyst.

The textural properties of the catalysts were obtained from nitrogen adsorption experiment. The surface area of the prepared Silica-SO_3H was determined to be 1102 m^2 g^{-1}. The pore diameter was calculated to be 2.87 nm by the BJH method. The H^+ exchange capacity was 0.20 mmol g^{-1}, which was determined by the potentiometric titration. The sulfur content in the Silica-SO_3H catalyst was determined to be 0.66 wt.% and the carbon content was determined to be 0.73 wt.% by elemental analysis. Thus the calculated mole ratio of H : S : C is equal to 1 : 1 : 2, which is consistent with the structure of propylsulfonic acid.

Effect of reaction temperature on the conversion of HMF into EMF

As HMF is the key intermediate for the one-pot conversion of fructose into EMF, the success of the preparation of EMF from HMF is crucial to being able to use the one-pot reaction. Therefore, the etherification of HMF into EMF was initially carried out in ethanol. Firstly, the etherification of HMF by ethanol was conducted at 80 °C, 100 °C and 120 °C in order to study the effect of the reaction temperature, and the results are shown in Fig. 2, from which, it was noted that reaction temperature had a remarkable effect on the etherification of HMF. A general rule of the effect of reaction temperature can be concluded as follows: the higher the reaction temperature, the higher the etherification rate. When the reaction temperature was set to 80 °C, HMF conversion and EMF yield reached 73.9% and 64.6% after 12 h. However, it only took 10 h to obtain a maximum EMF yield of 83.8% with HMF conversion

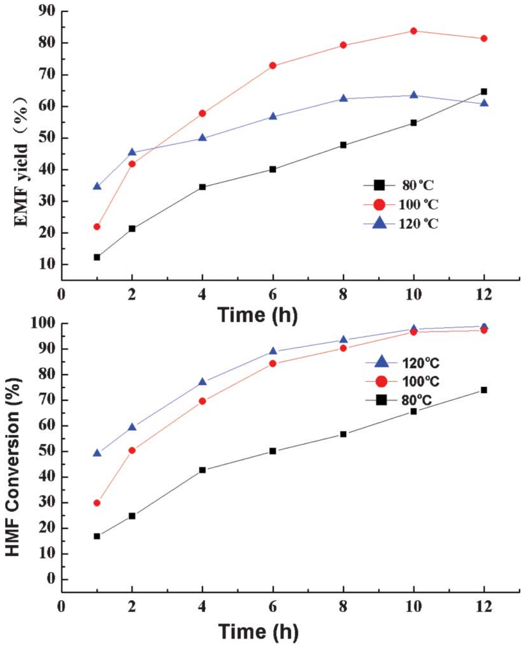


Fig. 2 Effect of reaction temperature on the etherification of HMF in ethanol. Reaction conditions: HMF (126 mg, 1 mmol) and Silica-SO_3H (200 mg) were added into 5 mL ethanol and then the reaction was carried out at a set temperature.

at 96.5%, when the reaction temperature was increased from 80 °C to 100 °C. Increasing the reaction temperature further to 120 °C, a 98.8% conversion of HMF after 12 h was the highest of the three different temperatures. However at 120 °C the EMF yield was only 60.8% after 12 h, which was the lowest for the three different reaction temperatures. Comparing the results of HMF conversion and EMF yield, the selectivity of EMF decreased with the increasing reaction temperature, which was due to higher temperatures causing side reactions that formed undesired byproducts. On the other hand, it was reported that HMF itself was not stable at high temperatures. In our experiments, some black, insoluble sediment by-product termed humins were observed when the reaction time was 4 h at 120 °C, which attenuated the EMF yield. Other research groups also observed the formation of humins, which was formed through the polymerization and cross-polymerization of HMF.[33–35] On the other hand, side products such as alkyl levulinates were favored to be formed at high temperature from the alcoholysis of HMF. Balakrishnan *et al.*[36] reported that ethyl levulinate was obtained in a 62% yield with 5 mol% H_2SO_4 at 120 °C for 30 h. Taking into account the effect of reaction temperature, 100 °C was chosen as the best reaction temperature for etherification of HMF into EMF.

Effect of catalyst loading on the etherification of HMF into EMF

Secondly, the influence of catalyst dosage on the etherification of HMF into EMF was investigated and the results are shown in Fig. 3. From Fig. 3, it is noted that increasing the catalyst loading led to an increase of EMF yield. Taking the early reaction stage at 1 h as an example, the yield of EMF yield was only 5.1% at 1 h with 100 mg Silica-SO_3H. Whereas, yields of 15.7%, 21.9% and 35.6% were reached with the amount of Silica-SO_3H being 150, 200 and 250 mg, respectively. A higher etherification rate of HMF with an increase in catalyst loading can be attributed to an increase in the availability and number of catalytically active sites. The maximum yields of EMF relied on the catalyst loading. A maximum EMF yield was obtained of 77.8% after 8 h with 250 mg Silica-SO_3H, and that increased to 83.8% yield with 200 mg Silica-SO_3H after 10 h. The reason might be that more catalyst loading accelerated the formation of EMF from HMF while it also favored the alcoholysis of HMF into alkyl levulinates, which offset the increase of EMF yield. In our experiment, the reaction mixture was analyzed by gas chromatography at the end of the reaction after 12 h, and ethyl levulinate yields were determined to be 23.4%, 14.8%, 10.5% and 7.9%, corresponding to the catalyst loading of 250 mg, 200 mg, 150 mg and 100 mg, respectively. These results verified the major by-product for the synthesis of EMF from HMF was caused by the alcoholysis of HMF. It was also noted that the maximum yield of EMF could not remain stable, when the reaction time was prolonged. The maximum EMF yield of 77.8% at 8 h slowly decreased to 69.7% after 12 h at 100 °C with a catalyst loading of 250 mg. These results indicate that the EMF product was also unstable during the reaction process. Yang *et al.*[37] have subjected EMF to heating at 160 °C for 1 h, and found that EMF was only recovered in an 82% yield, accompanying the formation of HMF and alkyl levulinates. Therefore, the appropriate amount of Silica-SO_3H was chosen as 200 mg in subsequent experiments if not otherwise indicated.

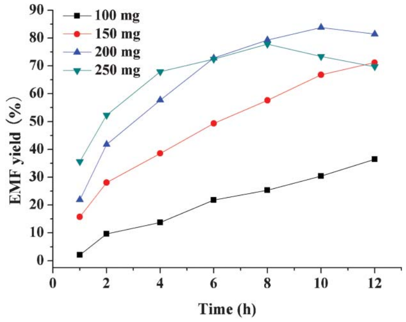


Fig. 3 The effect of catalyst loading on the etherification of HMF by ethanol. Reaction conditions: HMF (1 mmol) and a set amount of Silica-SO_3H were added into 5 mL ethanol and then the reaction was carried out at 100 °C.

One-pot dehydrative etherification of fructose into EMF

Although EMF was successful synthesized from HMF by the etherification with Silica-SO_3H as a catalyst, it would be desirable to synthesize EMF directly from fructose through a one-pot reaction, due to the dehydration of fructose into HMF and the etherification of HMF into EMF both requiring the acid catalyst. Therefore, synthesis of EMF from one-pot dehydrative etherification of fructose was carried out in the presence of Silica-SO_3H at 80 °C, 100 °C and 120 °C, respectively, and the yields of the intermediate HMF and the product EMF are shown in Fig. 4. Seeing the curves of HMF

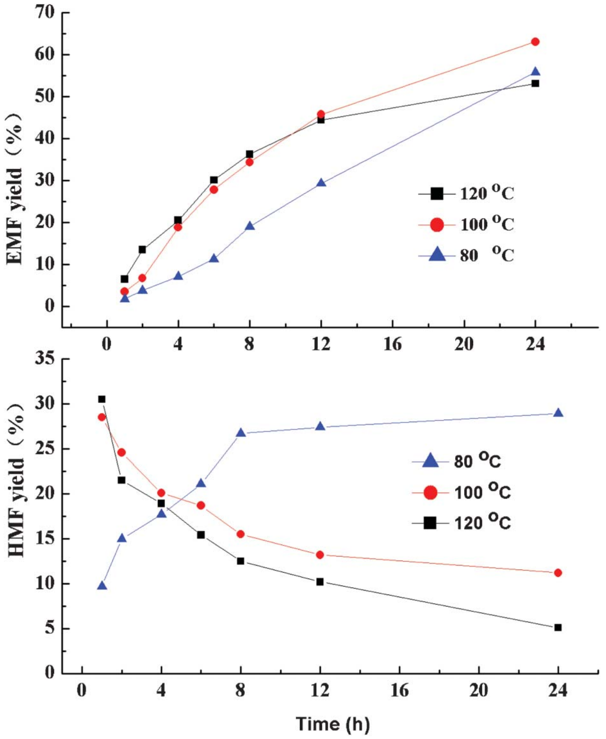


Fig. 4 Effect of reaction temperature on the one-pot dehydrative etherification of fructose in ethanol. Reaction conditions: fructose (180 mg, 1 mmol) and Silica-SO_3H (200 mg) were added into 5 mL of ethanol and then the reaction was carried out at a set temperature.

yields at different reaction temperatures, it was noted that HMF yields after 1 h decreased with the decrease of reaction temperature. The results indicated that a high temperature was beneficial to promote the dehydration of fructose into HMF, which was similar to the etherification of HMF into EMF as described above. Seeing the trends of HMF yields at different reaction temperatures, it was also found that the HMF yield at 80 °C firstly increased from 9.7% after 1 h to 26.7% after 8 h, and then kept stable around 27%. It indicated that the dehydration rate of fructose and the etherification rate of HMF were comparable at 80 °C. However, HMF yields decreased gradually at 100 °C and 120 °C, indicating that the etherification of HMF into EMF was faster than the dehydration of fructose into HMF. The yields of EMF gradually increased as the reaction time increased. The highest EMF yields reached were 55.9%, 63.1% and 53.1% at 80 °C, 100 °C and 120 °C, respectively. No fructose was detected at 24 h for the three different temperatures. The lowest EMF yield at 120 °C was also caused by the side reactions as described above. After the complete reaction at 100 °C and 120 °C, some insoluble humins were also observed, when the reaction mixture was diluted with water.

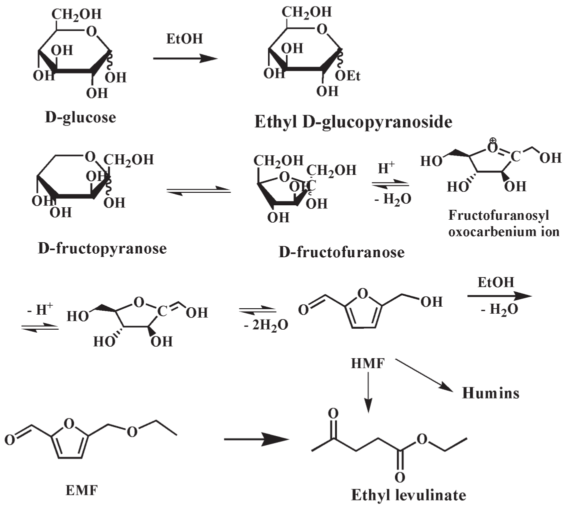
Conversion of various substrates in ethanol catalyzed by Silica-SO_3H

Various carbohydrates were used as substrates for the production of EMF in order to explore the scope of our catalytic system, and the results are shown in Table 1. As described above, an EMF yield of 63.1% was obtained from fructose after 24 h at 100 °C, with the HMF yield remaining at 11.2%. Then fructose based di- and polysaccharides (sucrose and inulin) were subjected to heating at 100 °C under the same reaction conditions as described for fructose. A high yield of EMF was obtained of 60.7% from inulin after 24 h, which was comparable with that from fructose. These results indicated that Silica-SO_3H could also effectively cleave the glycosidic bonds as well as showing catalytic activity for the dehydration of fructose and the etherification of HMF. Unfortunately, EMF yield only reached 34.9% after 24 h using sucrose, which was almost half of that from pure fructose. No sucrose was detected after the reaction. More importantly, the monosaccharides, fructose and glucose, also showed negligible detection. Interestingly, ethyl D-glucopyranoside (EGL) was also detected by HPLC and it was obtained in a yield of 45.0% using sucrose. Thus, it indicated that EGL was formed from the glucose part of sucrose. Furthermore, a high EGL yield was obtained of 91.7% after 12 h, when pure glucose was used as the substrate. Interestingly, an EGL yield of 85.9% after 12 h was also obtained when cellobiose was used. These results indicated that glycosylation of the hydroxyl group at C1 in glucose was readily promoted under the acidic conditions. However, the isomerization of glucose into fructose was much more difficult under the acidic conditions, which was generally accepted to be a key step for the effective synthesis of EMF in ethanol.[31] Unlike EMF, the product EGL is not a liquid fuel, but it has wide applications such as a biodegradable surfactant, a cosmetic humectant and a chemical intermediate.[38]

Table 1 The results of products yields using various carbohydrates in ethanol catalyzed by HSM-SO_3H^a

Entry	Substrate	Reaction time (h)	EGL yield (%)	HMF yield (%)	EMF yield (%)
1	Fructose	24	0	11.2	63.1
2	Sucrose	24	45.0	5.9	34.9
3	Inulin	24	0	6.5	60.7
4	Glucose	12	91.7	0	0
5	Cellobiose	12	85.9	0	0
6[b]	Fructose	24	ND	ND	ND
7[b]	Glucose	12	ND	ND	Nd

[a] Reaction conditions: Substrates (180 mg) and 200 mg Silica-SO_3H was added into 5 mL ethanol and the reaction was carried out at 100 °C.
[b] Other conditions were the same as above, unless the reaction was carried out without the catalyst. ND means not detected.



Scheme 2 Possible reaction pathway of the formation of EMF and EGL from hexoses in ethanol catalyzed by Silica-SO_3H.

According to previous results, the possible reaction pathway for the conversion of hexoses into ethyl D-glucopyranoside and EMF can be described as shown in Scheme 2. For ketoses such as glucose, it only catalyzed the glycosylation of glucose with ethanol to form ethyl D-glucopyranoside, which was similar to previous results reported that used Brønsted acid catalysts in methanol and butanol.[39,40] For the aldose, in the case of fructose, the release of one molecular water from D-fructopyranose under acidic conditions resulted in the formation of a fructofuranosyl oxocarbenium ion. The fructofuranosyl oxocarbenium ion could then convert into an enol furan intermediate by the release of H^+, which was subsequently dehydrated to molecular water to produce the intermediate HMF. Then, the hydroxyl group was activated by the acid catalyst, and substituted by ethanol to give rise to the final product, EMF. On the other hand, some byproducts such as humins and ethyl levulinates were also formed under acidic conditions.

Catalyst reuse experiments

Finally, the reusability and stability of the Silica-SO_3H catalyst was evaluated. The reuse experiment was carried out by a model reaction of the one-pot dehydrative etherification of fructose in ethanol at 100 °C, and the detailed procedures are described in the experimental section. After the completion of the reaction after 24 h with the use of fresh catalyst, the reaction mixture was filtered, and then washed with distilled water, ethanol and diethyl ether successively. The reused catalyst was placed under vacuum to remove the solvents at 80 °C over night. Then the recovered catalyst was added into a fresh solution of the reaction mixture and the second cycle was carried out under the same conditions. Fig. 5 shows the results from recycling Silica-SO_3H for six consecutive runs. It was found that the yields of EMF were kept almost stable. The EMF yield of the first run was 63.1%, and was 57.5% for the sixth time. Therefore, the Silica-SO_3H catalyst can be reused without losing its catalytic activity, which is favorable for the potential application in large scale synthesis and from the industrial point of view.

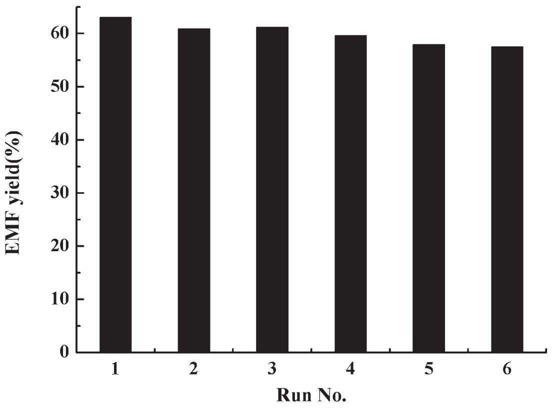


Fig. 5 Recycling experiments of the Silica-SO_3H catalyst.

Conclusions

In conclusion, synthesis of EMF from fructose based carbohydrates was efficiently developed through a one-pot reaction. The easily prepared silica supported sulfuric acid Silica-SO_3H catalyst showed a high catalytic activity for the etherification of HMF in ethanol with a high EMF yield of 83.8% at 100 °C. EMF was also successfully synthesized directly from fructose and inulin, with yields of 63.1% and 60.7%, respectively. However, Silica-SO_3H was inert for the synthesis of EMF from aldose based carbohydrates such as glucose. It can effectively catalyze the glycosylation of glucose into ethyl D-glucopyranoside with a high yield of 91.7%. Finally, reusability experiments demonstrated that Silica-SO_3H could be reused several times without losing its catalytic activity. This catalytic system provides a new catalytic process for the conversion of abundant renewable carbohydrates to high-heating value liquid biofuels and bio-based chemicals.

Acknowledgements

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