Supplementary Information for

Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon based solid acid

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1. Experimental

Materials

Fructose (99.8%), glucose (99.8%), p-toluene sulfonic acid (99.5%), dimethyl formamide (DMF, 99.5%), dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), and N-methyl pyrrolidone (N-MP) were purchased from shanghai chemicals company. 5-hydroxymethylfurfural (99.5%) was purchased from Alfa Aesar. H-β zeolite was purchased from Nankai University catalyst Co. Ltd. and Amberlyst-15 were purchased from Aladdin company. All reagents were commercial products of the highest purity available (>98%) and used as received without further purification.

Synthesis of the carbonaceous material (Glu-TsOH)

The preparation was similar to our previous report with a slight modification. In a typical synthesis, 4 g of glucose and 6 g of p-toluene sulfonic acid (TsOH) were mixed, ground, and placed in 100 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave was put into an oven of 180 °C and aged for one day. Then the resulting dark powder was collected from the autoclave and placed in the oven of 180 °C in open air for another day to remove the small organic compounds adsorbed on the surface of the material. After washing with hot water until sulfate ions were no longer detected and drying at 100 °C overnight, the catalyst was obtained and denoted as Glu-TsOH.

Synthesis of the reference material (AC-SO_3H)

A reference sample based on the active carbon was also prepared by using concentrated H_2SO_4 as sulfonate agent. A 30 mL Teflon liner, containing 1 g of activated carbon and 10 mL of concentrated H_2SO_4, was sealed into an autoclave and then put into an oven at 180 °C for 24 h. The obtained products were washed with hot distilled water (>80 °C) and filtered until no sulfate ions were detected in the filtration water, then dried at 100 °C overnight in air. This sample was denoted as and AC-SO_3H.

Catalyst characterization and products analysis

The catalyst was characterized by FT-IR. FT-IR spectrum was recorded over the range from 400 to 4000 cm^{-1} on a FT-IR (Nexus) after the catalyst was evenly mixed with KBr powder. 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). An auto-sampler (Agilent G1329A) was used to enhance reproducibility. HMF was analyzed with an ultraviolet detector (Agilent G1314B) and other products were analyzed with a refractive index detector (Agilent G1362A).

Dehydration of fructose to HMF

The mixture of fructose (0.5g), solvent (6 mL) and catalyst (0.4g) was stirred in a 50 ml single-necked bottle using a magnetic stirrer. N_2 gas was used for purging air outside the reactor to prevent the side reactions. The reactor was raised to reaction temperature and held at this temperature for a given period of time. After reaction, the mixture was centrifuged and the supernatant liquid was analyzed by an Agilent 1200 Series HPLC based on the external standard method. After each reaction, the catalyst was collected after centrifugation and dried at 180 °C for 24 hours to remove the volatile impurity. Then a new reaction was started as a new cycle with the used catalyst. This process was repeated several times, and the activity in each cycle was recorded.

2. FT-IR spectra of Glu-TsOH

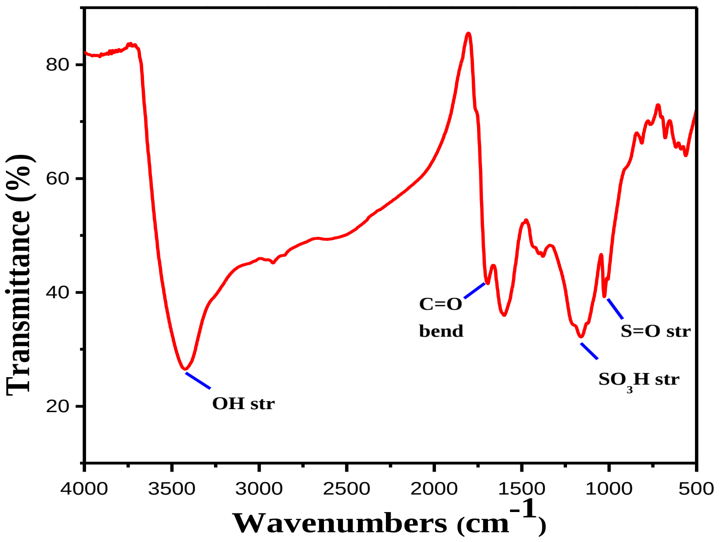

Fig. S1 FT-IR spectra of the Glu-TsOH.

The FT-IR spectrum of the Glu-TsOH is shown in Fig. S1. Upon hydrothermal carbonization of glucose and p- toluene sulfonic acid, this carbon material rich in functional groups such as phenolic hydroxyl, carbonyl, sulfonic acid groups, and carboxylic groups is obtained. The absorption band at 3427.7 cm^{-1} can be attributed to O-H stretching vibrations.[1,2] The bands at 1161.2 (SO_3-、stretching) and 1032 cm^{-1} (O=S=O stretching in SO_3H) in the FT-IR spectrum indicate that the carbonaceous material possesses SO_3H groups.[1-4] The other adsorption bands belong to carboxylic acid groups (1705 cm^{-1}), C=C double bands (1600 cm^{-1}).[1,2,5]

3. NH_3-TPD of Glu-TsOH

Temperature-programmed desorption of ammonia (NH_3-TPD) was performed on an apparatus PX200 (Tianjin Golden Eagle Technology Limited Corporation). The catalysts were charged into the quartz reactor, and the temperature was increased from room temperature to 120 °C over 1 h at a rate of 10 °C min^{-1} under a flow of N_2 (40 mL min^{-1}), and then the temperature was decreased to 90 °C. NH_3 was pulsed into the reactor at 90 °C under a flow of N_2 (40 mL min^{-1}) until the acid sites were saturated with NH_3. The adsorbed NH_3 was removed by a flow of N_2 (40 mL min^{-1}). When the baseline was stable, the temperature was increased from 150 °C to 750 °C at a rate of 10 °C min^{-1}. A blank measurement was conducted without adsorption of ammonia and after deducted the blank measurement, the NH_3-TPD curve of the Glu-TsOH was shown in Fig. S2.

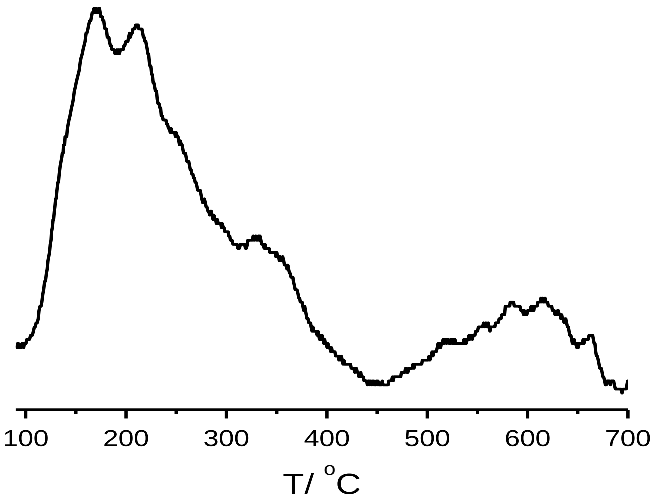

Fig. S2 The NH_3-TPD curve of the Glu-TsOH.

4. **Titration results of every functional groups over Glu-TsOH**[6,7]

The titration method of the surface functional groups over Glu-TsOH was similar to the references[6,7] and the detailed method was as following.

The measurement of the total functional groups (-SO_3H, -COOH and -OH groups): a sodium hydroxide aqueous solution (0.05 mol L^{-1}, 30 mL) was added to a catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid (0.05 mol L^{-1}) aqueous solution using phenolphthalein as an indicative.

The contents of -SO_3H plus -COOH groups: a sodium bicarbonate aqueous solution (0.05mol L^{-1}, 30 mL) was added to a catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid (0.05mol·L^{-1}) aqueous solution using phenolphthalein as an indicative.

The content of -SO_3H group: a sodium chloride aqueous solution (0.05mol L^{-1}, 30 mL) was added to a catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a sodium hydroxide (0.05mol·L^{-1}) aqueous solution using phenolphthalein as an indicative.

According to the above titration results, the content of -OH groups = the content of the total functional groups – the content of -SO_3H plus -COOH groups; the content of -COOH groups = the content of -SO_3H plus –COOH groups – the content of -SO_3H groups. The calculated results are listed in Table S1.

Table S1 The density of every functional group

Sample	The functional groups densities (mmol/g)		
	SO_3H	COOH	OH
Glu-TsOH	1.3	0.6	0.1
AC-SO_3H	0.6	0.4	1.7

5. References

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