Electronic Supplementary Material (ESI) for Green Chemistry.

Conversion of carbohydrates to furfural via selective cleavage of carbon-carbon bond: cooperative effect of zeolite and solvent

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1. Materials

Cellulose, inulin, starch, sucrose, maltose, D-glucose, D-fructose, D-xylose, D-arabinose, 5-hydromethylfurfural (HMF), formic acid (FA) and levulinic acid (LA) were purchased from Aladdin. γ-valerolactone (GVL), γ-butyrolactone (GBL), 1,4-dioxane, gluconic acid, H_2SO_4 (98%), Amberlyst-15, $AlCl_3$ and γ-Al_2O_3 were purchased from Sinopharm Chemical Reagent Co., Ltd.. All the above agents were utilized without further purification. Hβ, HY, H-Mordenite and HZSM-5 zeolite were purchased from The Catalyst Plant of Nankai University.

2. Experiments

2.1 The computational formula

The conversion of sugars and the yield of the products were quantified according to the following equations:

$$Conversion = \frac{mol\ of\ sugar(inlet) - mol\ of\ sugar(outlet)}{mol\ of\ sugar(inlet)} \times 100\%$$

$$Yield = \frac{mol\ of\ one\ product\ produced}{mol\ of\ theoretical\ product\ value} \times 100\%$$

2.2 Procedures for the catalyst recycling

After the first run was completed, the reaction products were centrifuged for 10 min to separate the Hβ zeolite from the solutions. The Hβ zeolite was washed with GBL-water (5 wt%) thoroughly and dried at 100 °C for 12 h. Then the dried Hβ zeolite was used as the catalyst for the next run.

2.3 Procedures for the dealuminizing of zeolite

0.5 g Hβ zeolite was added in 50 ml HNO_3 (6 M) aqueous solution, refluxing for 4 h at 80 °C. Then the mixture was cooled and the Hβ zeolite was separated. The Hβ zeolite was washed for 5 times with water and then dried at 100 °C for 12 h. Then the dried zeolite was caclined in air at 550 °C for 4 h.

2.4 Procedures for preparing the samples for FTIR

The process of preparing samples for FTIR: 0.2 g zeolite (Hβ or HY) and 0.5 g sugar was added in 9.5 g water or 1,4-dioxane/water(9 g: 0.5 g) solvent. The mixture was stirred vigorously for 4 h at room temperature. The zeolite was separated and washed with the solvent for 2 times, and then dried for 6 h at room temperature.

3 Catalyst characterizations

3.1 X-ray diffraction (XRD) measurements

Powder X-ray diffraction (XRD) patterns were obtained on a D8 ADVANCE A25 X-ray diffractometer (Germany), with Cu Kα radiation at 30 kV and 10 mA. The X-ray patterns were recorded in 2θ values ranging from 5° to 80° with a scanning speed of 4 °/min.

3.2 Fourier transforms infrared spectroscopy (FTIR)

The FT-IR spectra were measured on a BRUKER TENSOR27 FTIR spectrophotometer (Bruker, Germany), equipped with a deuterium triglycine sulfate (DTGS) detector. The powder samples were mixed with KBr and pressed into translucent disks at room temperature. The spectra were recorded in the range of 400-4000 cm^{-1}.

3.3 IR spectra of adsorbed pyridine (Py-IR)

Py-IR was performed in Vertex 70 (Bruker) FT-IR spectrophotometer with a deuterium triglycine sulfate (DTGS) detector. For each run, the sample was pressed into self-supporting wafers and degassed in vacuum at 300 °C for 1 h followed by exposure to pyridine vapor. Subsequently, the Py-IR spectra were measured at 200 °C after applying vacuum for 30 min. The quantification of Brønsted and Lewis acid sites was estimated from the integrated area of adsorption bands at ca. 1540 and 1450 cm^{-1}, respectively.

3.4 NH_3-TPD of various zeolites

The acid amounts of zeolites were measured with thermal programmed desorption (TPD) of NH_3 on Auto Chem. Ⅱ2920 equipment (Micromeritics, USA) with a mass spectra. The sample was adsorbed with NH_3 until saturation. Then, the zeolite was flushed with helium at 100 °C for 0.5 h to remove the physisorbed NH_3. TPD was conducted from 100 °C to 800 °C at a heat rate of 10 °C / min.

3.5 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The Si/Al of various zeolites was analyzed by PerkinElmer Optima 2100 DV.

3.6 Thermo-gravity (TG) experiments

Thermo-gravity (TG) experiments of used catalyst were performed on a Mettler Toledo TGA/SDTA 851 instrument (air atmosphere 50 ml/min and heating rate of 10

°C/min). Prior to the test, both the fresh reduced and used catalysts were dried in air at 100 °C for 24 h.

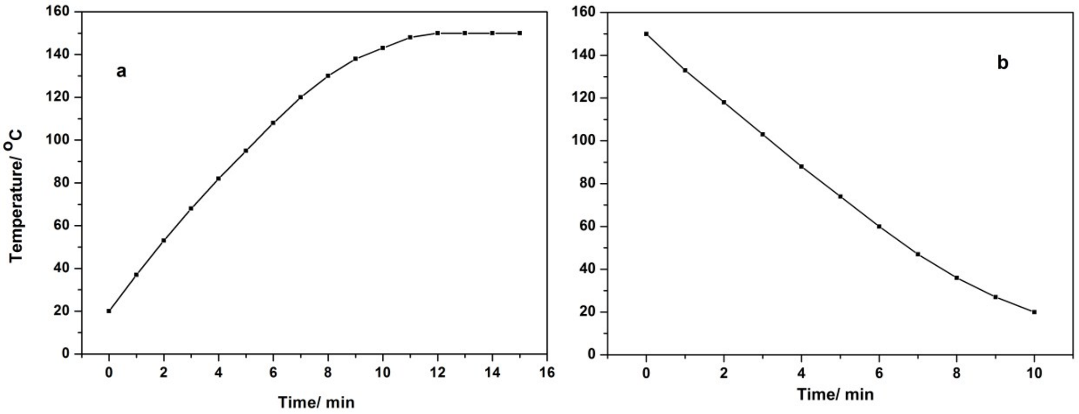

Figure S1 The heating rate (a) and cooling rate (b) of the reactions

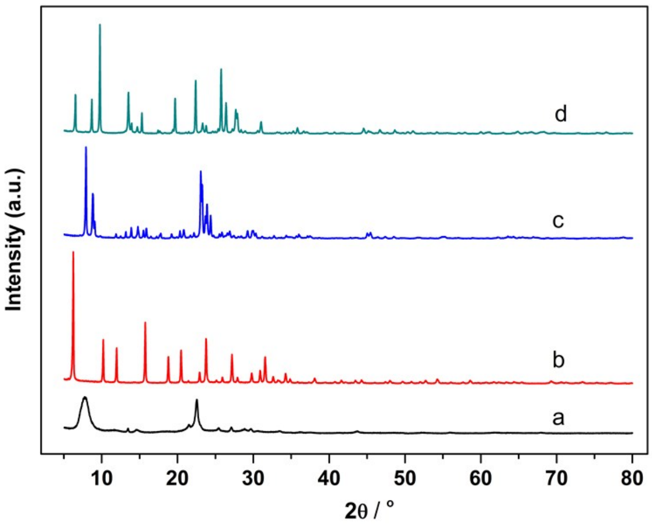

Figure S2 The XRD patterns of (a) Hβ, (b) HY, (c) HZSM-5, (d) H-Mordenite

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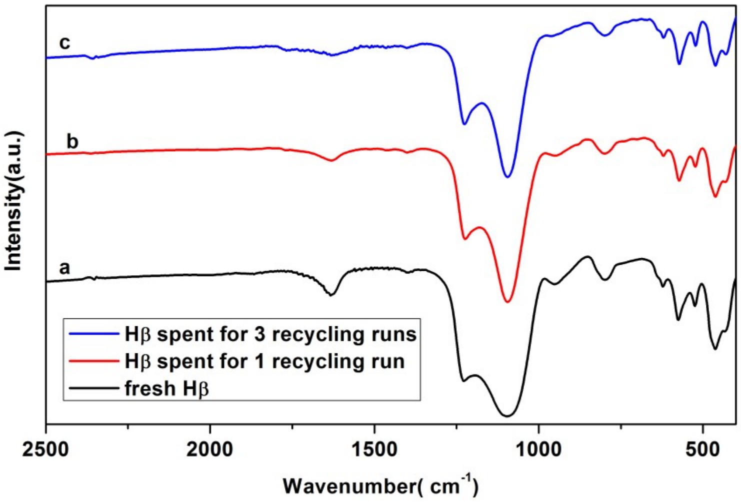

Figure S3 The FTIR spectra of (a) fresh Hβ, (b) Hβ spent for 1 run, (c) Hβ spent for 3 recycling runs

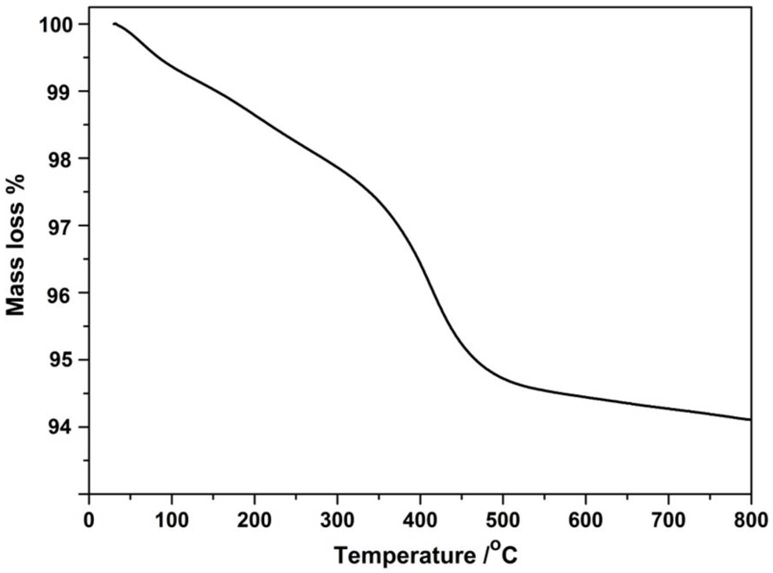

Figure S4 Thermo-gravity profile of recycled Hβ zeolite

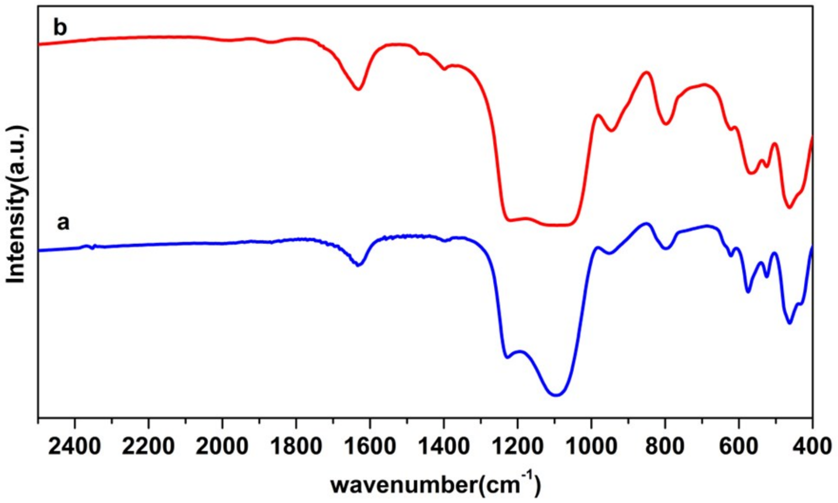

Figure S5 The FTIR spectra of (a) Hβ, (b) Hβ+arabinose+water

Table S1 The loss of formaldehyde in the reactions [a]

Entry	Catalyst	Substrate	HCHO loss ratio%
1[b]	Hβ	Formaldehyde	5.6
2[c]	Hβ	Formaldehyde + furfural	6.5
3[d]	Hβ	Formaldehyde + arabinose	30.8
4[d]	-	Formaldehyde + fructose	49.1
5[d]	-	Formaldehyde + glucose	43.6

[a]: 0.1 g Hβ zeolite, 10 g substrates and GBL-water mixture, water content 5 wt%, 150 °C, 1 h; [b]: 0.1 g formaldehyde; [c]: 0.1 g formaldehyde, 0.3 g furfural; [d]: 0.1 g formaldehyde, 0.5 g sugar.

Table S2 The physicochemical properties of various zeolite catalysts

Catalyst	Si/Al [a]	Acid amount (mmol·g^{-1} catalyst) [b]	L acid /B acid mol ratio [c]
Hβ	25	0.366	3.02
HY	6	0.391	2.18
H-Mordenite	17	0.12	1.03
HZSM-5	32	0.134	0.63

[a]: the Si/Al of various zeolites was determined by ICP-OES; [b]: the acid amount was determined by NH_3-TPD characterization; [c]: the acid type was determined by pyridine adsorption FTIR characterization.

Table S3 The conversion of HMF in GBL-water [a]

Entry	Substrate	T/ °C	Conversion%	Furfural yield %
1	HMF	150	56.1	Not detected
2	HMF	160	75.3	Not detected

[a]: 0.1 g Hβ catalyst, 0.5 g HMF, 0.5 g water, 9 g GBL, reaction time 1 h, 2 MPa N_2.

Table S4 The yield of arabinose in the reactions [a]

Entry	substrate	T/ °C	t/ min	Arabinose yield %
1	fructose	150	30	2.8
2	glucose	150	60	2.7

[a]: 0.1g Hβ catalyst , 0.5 g substrate, 0.5 g water, 9 g GBL, 2 MPa N_2.

Table S5 The conversion of arabinose in GBL-water over Hβ catalyst [a]

Entry	Substrate	T/ °C	t/ h	Conversion%	Furfural yield %
1	arabinose	150	1	99.9	76.8

[a]: 0.1 g Hβ catalyst , 0.5 g arabinose, 0.5 g water, 9 g GBL, 2 MPa N_2.

Table S6 IR data for D-fructose [1]

D-fructose (cm^{-1})	Possible assignment	D-fructose (cm^{-1})	Possible assignment
3422	νO-H	1079	νCO+δCC
1633	δ H_2O	1053	νCO
1470	δCH_2+ δOCH +δCCH	978	νCO+δCCO
1453	δOCH +δCCH	921	νCO+δCCH+νasy (ring of fructose)
1399	δOCH+ δCOH+δCCH	867	νCC+δCCH+δCH (ring of fructose)
1342	δCCH+ δCOH	817	δCH
1179	δOCH +δCCH	779	τCO+δCCO+δCCH
1147	νCO+νCC+δCCC (pyranose)	701	δCCO+τCO+δOCO
1095	νCO+νCC		

ν: stretching vibration; δ: bending vibration ; τ: twisting vibration.

Table S7 The conversion of arabinose and xylose to furfural over Hβ zeolite [a]

Entry	substrate	Solvent	conv. %	Furfural yield mol%	Others% [c]
1	arabinose	water	42.7	12.1	4.5
2	xylose	water	51.2	19.4	4.1
3[b]	arabinose	1,4-dioxane-water	97.1	60.5	2.3
4[b]	xylose	1,4-dioxane-water	99.7	73.2	3.1
5[b]	arabinose	GBL-water	99.9	76.8	6.5
6[b]	xylose	GBL-water	99.9	87.2	4.5

a: 0.5 g Hβ zeolite, 0.5 g substrate, 9.5 g water, 150 °C, t=1 h; b: 0.5 g substrate, 0.5 g water, 9 g 1,4-dioxane or GBL, 0.1g Hβ zeolite ; c: formic acid, acetic acid and propionic acid.

Table S8 The comparison of furfural degradation in water and GBL-water [a]

Entry	Substrate	Solvent	Furfural loss ratio %
1	Furfural	Water	25.2%
2	Furfural	GBL-water (5 wt%)	1.5%

a: 150 ^{o}C, 1 h, 0.1 g Hβ, 2 MPa N_2; 3 wt% furfural solution 10 g.

Table S9 The recycling of Hβ zeolite for converting fructose and glucose[a]

Entry	Recycling runs	sugar	T/^{o}C	Conv.%	Furfural yield %
1	0	Fructose	150	99.8	63.5
2	1	Fructose	150	99.9	61.8
3	2	Fructose	150	99.9	59.5
4	3	Fructose	150	99.9	57.1
5[b]	4	Fructose	150	99.9	62.1
6	0	Glucose	150	99.9	56.5
7	1	Glucose	150	99.9	54.1
8	2	Glucose	150	99.9	53.2
9	3	Glucose	150	99.9	48.9
10[b]	4	Glucose	150	99.9	53.2

[a]: 0.1 g Hβ catalyst; 10 g fructose or glucose/GBL-water solution for each run, water concentration 5 wt%, fructose or glucose concentration 5 wt%; reaction time: 1 h for fructose conversion, 2 h for glucose conversion, 2 MPa N_2; [b]: the Hβ zeolite after 3 recycling runs was calcined at 600 ^{o}C for 2 h(air atmosphere).

Table S10 The conversion of fructose/glucose mixture [a]

Entry	Substrate	Furfural yield %
1	0.146 mmol fructose + 0.146 mmol glucose	59.7%

a: 150 ^{o}C, 2 h, 0.1 g Hβ; 10 g sugar GBL-water solution with water content 5 wt%.

Table S11 The effect of pressure on the conversion of fructose into furfural in GBL-water[a]

Entry	P/ MPa	T/°C	Conv.%	Furfural yield %
1	0.1	150	99.8	59.6
2	1	150	99.9	62.8
3	1.5	150	99.9	63.9
4	2	150	99.9	63.5
5	2.5	150	99.9	62.1

[a]: 0.1 g Hβ catalyst; 10 g fructose e/GBL-water solution for each run, water concentration 5 wt%, fructose concentration 5 wt%; reaction time: 1 h for fructose conversion,

Notes and references

1. J. Y. Guo and X. M. Zhang, *Carbohyd. Res.*, 2004, **339**, 1421-1426.