Selective Yields of Furfural and Hydroxymethylfurfural from Glucose in Tetrahydrofuran over Hβ Zeolite†

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1 Catalyst characterization

1.1 Procedures for XRD test

The crystalline structure of catalysts were characterized by X-ray diffraction (XRD) (X Pert Pro MPD with Cu Kα radiation, Philip) operated at 40 kV and 30 mA. The scanning angle (2θ) ranged from 5° to 80° and they were recorded with 0.0167° steps.

1.2 Procedures for TG-DTA test

The thermo-gravity - differential thermal analysis (TG-DTA) results of used catalyst was performed on a STA HP/2 instrument (air atmosphere 50 mL/min and heating rate of 10 $Kmin^{-1}$). Prior to the test, the used catalyst was dried in air at 393 K for 24 h.

1.3 Procedures for Py-IR test

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 573 K for 1 h followed by exposure to pyridine vapor. then, the Py-IR spectra were measured at 473 K after applying vacuum for 30 min. The quantification of Brønsted and Lewis acid sites was estimated from the integrated area of adsorption bands at 1540 cm^{-1} and 1450 cm^{-1} respectively.

1.4 Procedures for BET test

The Brunauer-Emmett-Teller (BET) surface area, external surface area, pore volume were determined by nitrogen adsorption at 77 K using a QUADRASORB SI analyzer equipped with QuadraWin software system. All samples were degassed at 573 K for 8 h before adsorption measurement. After measurement, surface areas were calculated by the BET method and micropore volumes were calculated with the T-plot method.

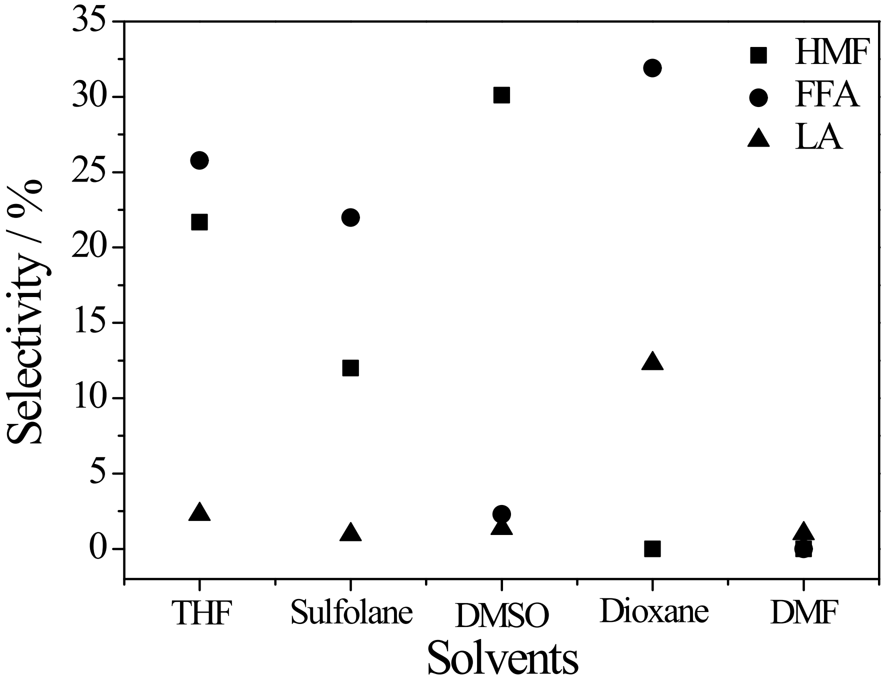
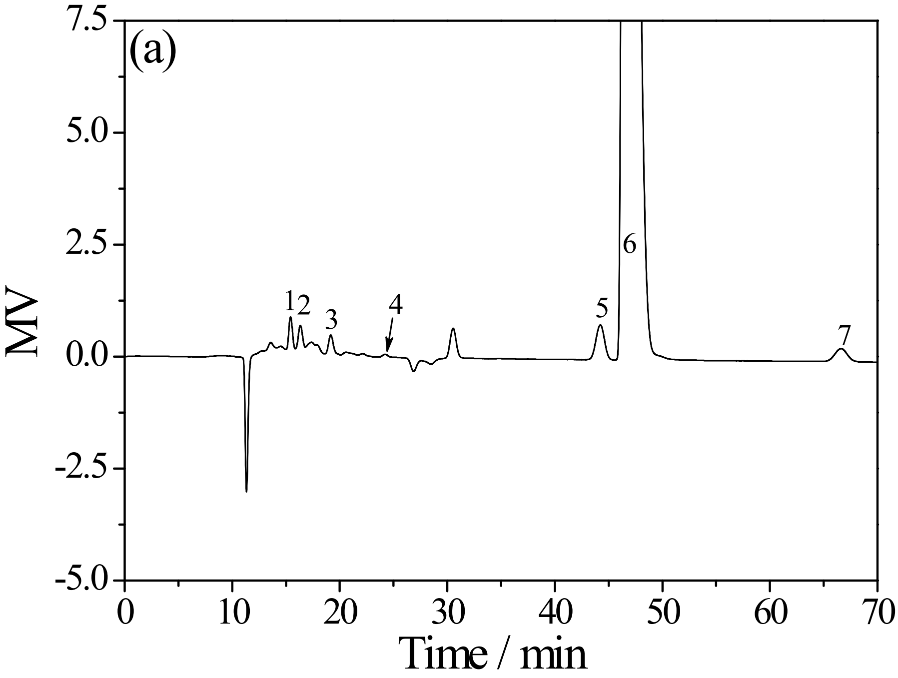


Fig. S1 Selectivities of different products in various solvents.

Reaction conditions: 0.5 g glucose, 0.1 g Hβ zeolite, 9.5 g solvent, 453 K, 120 min.



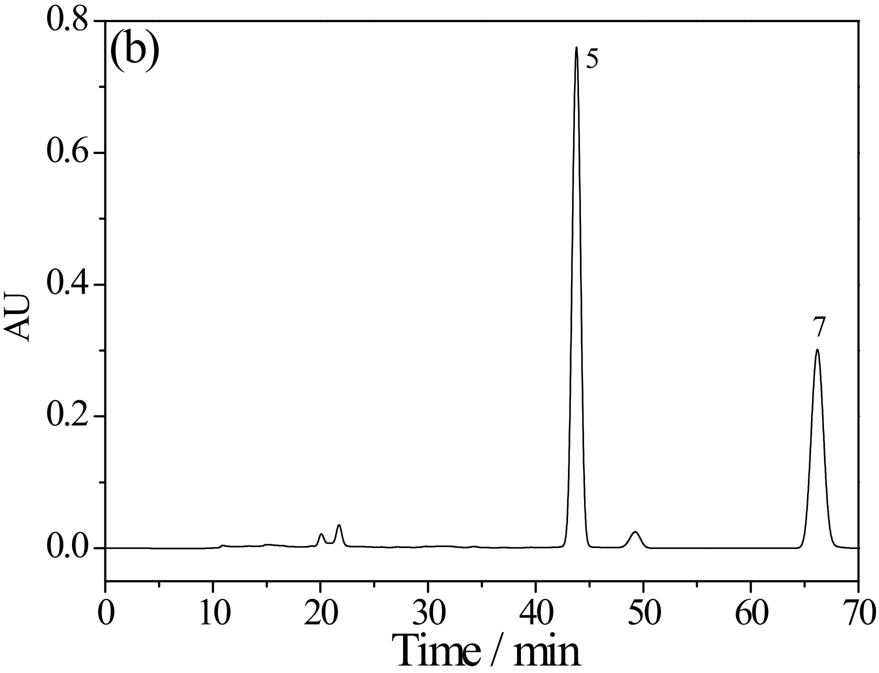


Fig. S2 HPLC chromatograms of the products produced from glucose in THF/water.

(a) refractive index detector, (b) UV detector. 1) glucose, 2) fructose, 3) formic acid, 4) LA, 5) HMF, 6) THF, 7) FFA.

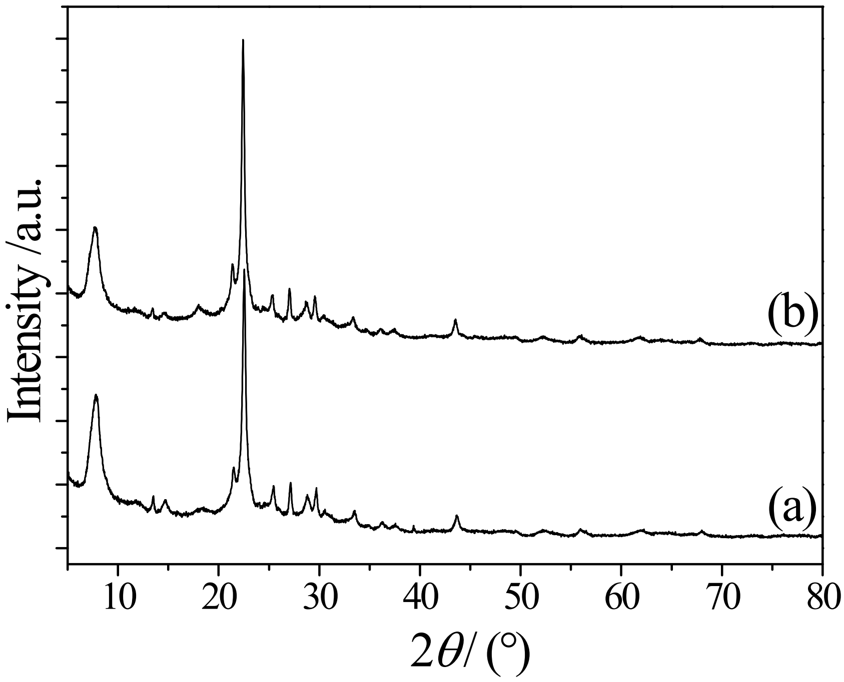


Fig. S3 XRD patterns of Hβ zeolite before and after reaction. (a) fresh, (b) after reaction.

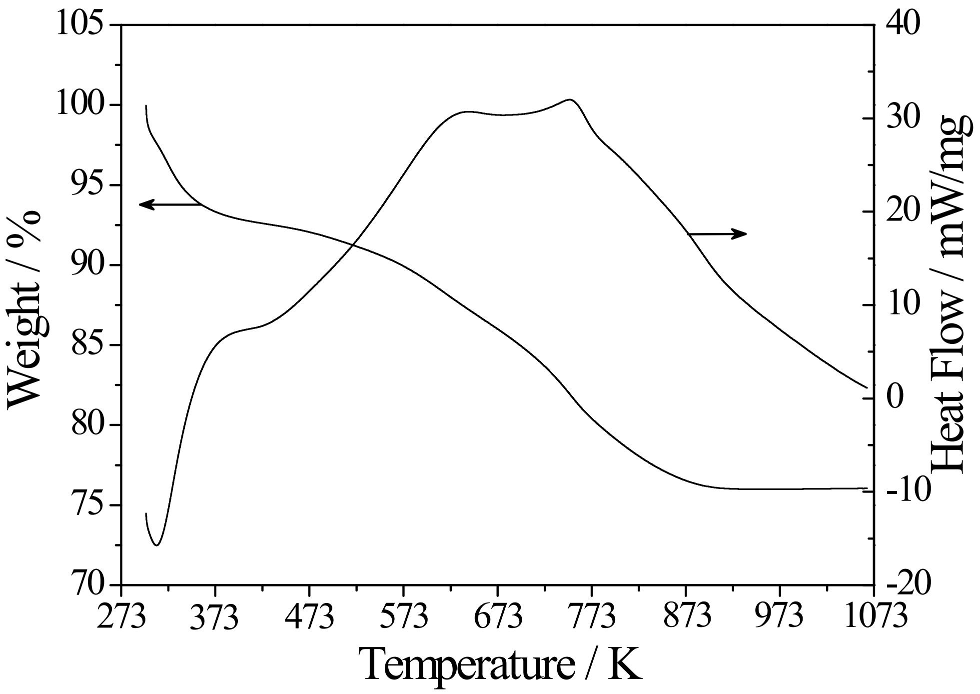


Fig. S4 TG-DTA analysis of the used Hβ zeolite.

Table S1 Physicochemical properties of Hβ zeolite before and after reaction.

Catalyst	A_{BET} / m²/g	A_{ext} / m²/g	V_{mic} / cm^3/g	Pore Size / Å
Before	457.18	114.99	0.18	27.08
After	293.22	95.04	0.10	25.92

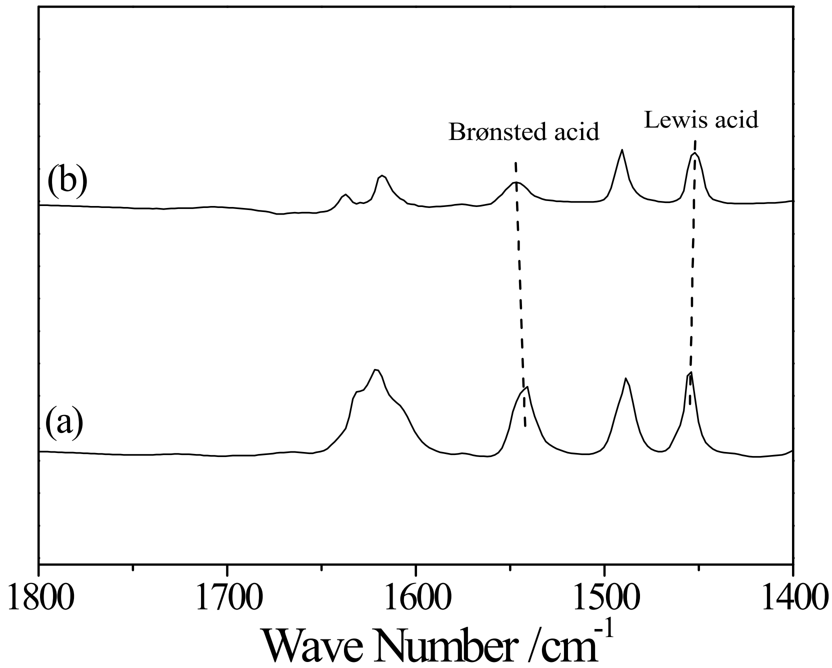


Fig. S5 Py-IR spectrum of Hβ zeolite before (a) and after reaction (b).

Table S2 Comparison of Lewis acid and Brønsted acid content of Hβ zeolite before and after reaction.

Catalyst	Acid amount (μmol·g^{-1} catalyst)		Lewis acid/Brønsted acid
	Lewis Acid	Brønsted Acid	
Before	254.9	490.7	0.52
After	139.9	146.2	0.96

Table S3 Typical production of FFA from pentose and hexose in various solutions.

No.	Substrate	Catalyst	Solution	Yield / %	Pros and Cons	Ref.
1	xylose	H_2SO_4	[BMIM]Cl	13.0	Simple catalyst but with corrosive and unrecyclable. Lower yield and valuable solution.	[1]
2	xylose	$Sn_{0.625}Cs_{0.5}PW$	$DMSO/H_2O$	63.0	Higher yield. Complex and valuable catalyst.	[2]
3	xylose	$CrPO_4$	THF/H_2O	67.0	Higher yield. Poisonous catalyst.	[3]
4	xylose	HCOOH	H_2O	74.0	Higher yield and simple solution. Corrosive and unrecyclable catalyst.	[4]
5	xylose	SAPO-34	GVL/H_2O	40.0	Simple system.	[5]
6	switchgrass	SAPO-34	GVL/H_2O	31.0	valuable solution.	[5]
7	xylose	[EMIM][HSO_4]	toluene	84.0	Higher yield. Valuable catalyst and poisonous solution.	[6]
8	corncob	H_2SO_4	H_2O	69.0	Higher yield, simple system and simple solution. Corrosive	[7]

					and unrecyclable catalyst.	
9	xylose	Hβ	GBL/H_2O	87.2	Higher yield and	[8]
10	arabinose	Hβ	GBL/H_2O	76.8	simple system.	[8]
11	glucose	Hβ	GBL/H_2O	53.2	Catalyst needs dealuminizing procedures.	[8]
12	glucose	Hβ	GVL/H_2O	33.0	Simple system. Valuable solution.	[9]
13	glucose	SC-CaCt-700	GVL/H_2O	18.6	Simple system. Lower yield, complex catalyst and valuable solution.	[10]
14	fructose	Hβ	GBL/H_2O	63.5	Higher yield and simple system.	[8]
15	cellulose	Hβ	GVL/H_2O	38.5	Catalyst needs dealuminizing procedures.	[8]
16	glucose	Hβ	THF/H_2O	35.2	Simple system. Recyclable catalyst and solution.	This work

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