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Author(s)	Kobayashi, Hirokazu; Yokoyama, Haruka; Feng, Bo et al.
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Dehydration of sorbitol to isosorbide over H-beta zeolites with high Si/Al ratios

Hirokazu Kobayashi,[a] Haruka Yokoyama,[a,b] Bo Feng[a] and Atsushi Fukuoka[a,*]

[a] Catalysis Research Centre, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

[b] Department of Chemistry, Faculty of Science, Hokkaido University, Kita 10 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.

Materials and characterisation

Details of Hβ zeolites used in this study are shown in Table S1, and those for other zeolitic materials are as follows: HY(2.55), Zeolyst; HUSY(40), Zeolyst; HUSY(250), Tosoh; HZSM-5(12.5), Clariant; HZSM-5(45), Clariant; HZSM-5(750), Tosoh; HMOR(15), Tosoh; HMOR(45), Catalysis Society of Japan; HMOR(120), Tosoh. All the zeolites were calcined at 823 K for 8 h prior to use. Nafion SAC-13, silica-supported fluorinated sulfonic resin, was purchased from Aldrich. Catalysts were characterised by N_2 adsorption (BEL Japan, BEL-Sorp Mini), NH_3-temperature programed desorption (BEL Japan, BEL-CAT, mass spectrometer, m/z = 16), X-ray diffraction (XRD; Rigaku, Ultima IV, Cu Kα), energy dispersive X-ray spectroscopy (EDX; Shimadzu, EDX-720) and total carbon analysis (Shimadzu, SSM-5000A).

Table S1 Hβ zeolites used in this study.

Si/Al	Company	Product name	BET specific surface area /m^2 g^{-1}	External surface area[a] /m^2 g^{-1}	Micropore volume[a] /cm^3 g^{-1}
12.5	Clariant	H-BEA-25	490	130	0.18
17.5	Clariant	H-BEA-35	590	41	0.26
25	Clariant	H-BEA-50	650	70	0.25
50	Tosoh	HSZ-960-HOA	670	11	0.29
75	Clariant	H-BEA-150	610	85	0.25
250	Tosoh	HSZ-980-HOA	610	23	0.26

[a] *t*-Plot method (second line: t > 1 nm).

Dehydration of sorbitol

The dehydration reaction was conducted with no solvent in a three-necked flask (100 mL; Fig. S1). The melting points of sorbitol (m.p. 368 K) and expected products, 1,4-sorbitan (385 K) and isosorbide (336 K), are all higher than our reaction temperature (400 K), which enables us to use the

neat conditions. Sorbitol (182 mg) and catalyst (50 mg) were ground together in a mortar, and the solid mixture was put into the flask. The flask was immersed in an oil bath at 403 K, and the reaction was continued for 2 h with stirring by a spin bar under a reduced pressure of 700 hPa. This reaction similarly can be performed in open air in this scale, but we use 700 hPa to keep the conditions constant. Temperature of the reaction mixture was measured by a thermocouple [Chino; ø1.0, K-type, class 1, coated with polytetrafluoroethylene (PTFE)], which was 400 K. After the reaction, a 20 mL of water was added to the mixture at room temperature to extract products, and the aqueous phase was analysed by HPLC [Shimadzu LC10-AT*VP*, refractive index and ultraviolet (210 nm) detectors] with a Shodex Sugar SH1011 column (ø8 × 300 mm, mobile phase: water 0.5 mL min^{-1}, 323 K) and a Phenomenex Rezex RPM-Monosaccharide Pb++ column (ø7.8 × 300 mm, mobile phase: water 0.6 mL min^{-1}, 343 K). Products were identified with LC/MS and NMR (^{1}H, ^{13}C, COSY, HMQC, HMBC).

Reuse experiments were performed with the following procedure. After the reaction, solid catalyst was separated from aqueous solution by filtration (PTFE membrane, 0.1 μm) and washed with water. After drying at 383 K for 2 h, the solid sample was calcined at 823 K for 8 h. The recovered catalyst was accumulated by repeating the same reaction, as a few per cent of catalyst was lost in handling. The reactivated solid catalyst of 50 mg was used in the next reaction.

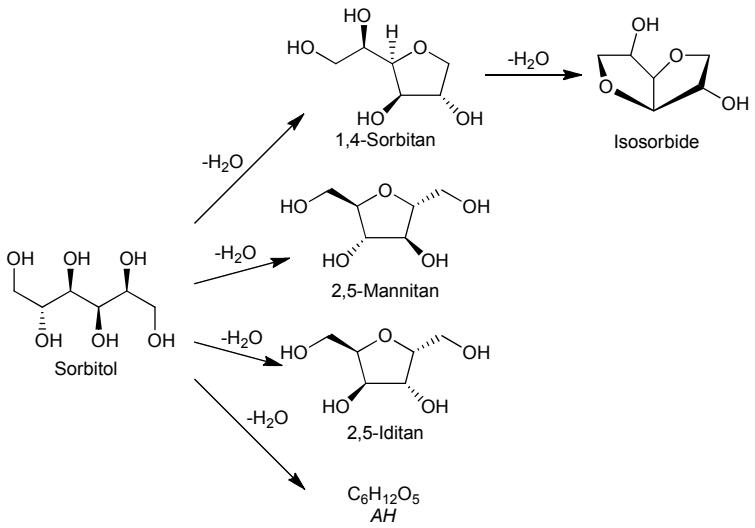
Modification of external surface of Hβ(75) with triphenylsilane

Acid sites on the external surface of Hβ(75) were modified according to literatures.[S1] Hβ(75) of 0.65 g was dried at 573 K for 1 h under He (40 mL min^{-1}) in a Pyrex fixed-bed flow reactor, and cooled down to 373 K. Triphenylsilane (Ph_3SiH) was vaporised at 343 K using a bubbler and adsorbed onto Hβ(75) at 373 K for 1 h, and subsequently physically-adsorbed triphenylsilane was removed at 373 K for 1 h. The reactor was heated to 873 K by 2 K min^{-1} and kept at the temperature for 1.5 h to decompose the silane compound. Carbon was removed at 873 K for 1.5 h under a gas mixture (O_2/He = 0.25, total 50 mL min^{-1}). This sequence was repeated three times to completely cover external acid sites, and a surface-modified Hβ(75) of 0.62 g was recovered.

Discussion on the activity difference among various types of zeolites

Since the acid amounts of Hβ(50), HUSY(40), HZSM-5(45) and HMOR(45) are similar (300–400 μmol g^{-1}),[S2] the activity difference may be due to acid strength or specific crystalline structure of zeolite. We have concluded that the latter factor is crucial for determining the activity as described below. The acid strength can be shown as the enthalpy change ($\Delta H°$) of ammonia desorption from a zeolite in NH_3-TPD, and $\Delta H°$ is uniquely determined by the type of zeolite with almost no dependence on Si/Al ratio.[S2] $\Delta H°$ values for Hβ, HUSY, HZSM-5 and HMOR are *ca.* 130, 120–135, 135 and 150 kJ mol^{-1}, respectively,[S3] while the activity order is Hβ > HUSY > HZSM-5 > HMOR,

showing limited correlation. Furthermore, Nafion SAC-13 with significantly different acid strength ($\Delta H°$ = 160 kJ mol^{-1})[S4] shows good catalytic activity under the same conditions (99% conversion of sorbitol at 400 K for 2 h; *this catalyst suffers from coking after the reaction, but has no regeneration way*). Accordingly, the acid strength is a minor factor for the catalytic performance in the range; instead the high catalytic activity and selectivity of Hβ is probably specific to the crystalline structure. Since the major reaction sites of Hβ are inside of pores, we focus on the pore structures of respective zeolites. Both Hβ (*BEA) and HUSY (FAU) have three-dimensional twelve-membered rings with large pore diameters (6.6×6.7 and 7.4×7.4 Å, respectively) that allow smooth diffusion of substrate and products. The major differences are slightly larger pore size and supercages of HUSY. The large space of HUSY may promote side-reactions because HUSY provides a large amount of by-products such as 2,5-mannitan and 2,5-iditan, produced by 2,5-dehydration. Specifically, 2,5-dehydrations (S_N2 reactions on secondary carbon centres) for side-reactions requires larger spaces than those for 1,4- and 3,6-dehydrations (S_N2 reactions on primary carbon centres) for the production of isosorbide. HMOR (MOR) is also a twelve-membered ring zeolite (6.5×7.0 Å) but has virtually a one-dimensional pore structure. Thus, the diffusion is slower and it is well known that MOR is seriously susceptible to coking in acid-catalysed reactions. HZSM-5 (MFI) is a ten-membered ring zeolite (5.3×5.6 Å) in which diffusion of the sugar compounds is limited, resulting in a low reaction rate. Accordingly, Hβ is the best catalyst for this reaction.



Scheme S1 Formation routes of products in the dehydration of sorbitol. Coke may be formed from any compounds.

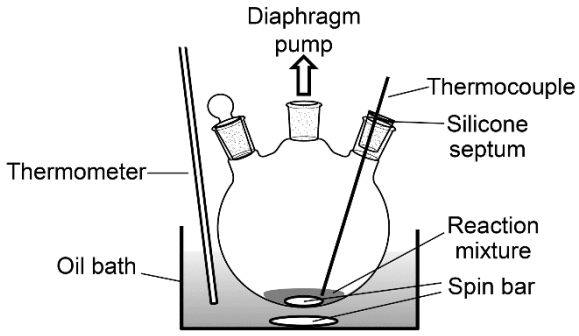


Fig. S1 Diagram of the reaction apparatus.

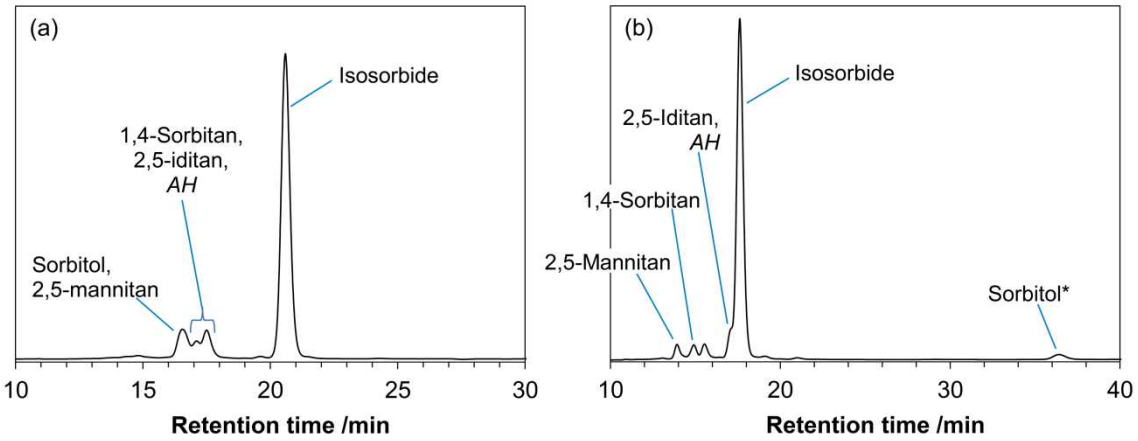


Fig. S2 HPLC charts of the dehydration of sorbitol by Hβ(75). (a) Shodex Sugar SH-1011 column, (b) Phenomenex Rezex RPM-Monosaccharide Pb++ column. *Retention time of sorbitol ranges from 35 to 45 min, depending on the conditioning of the Pb column.

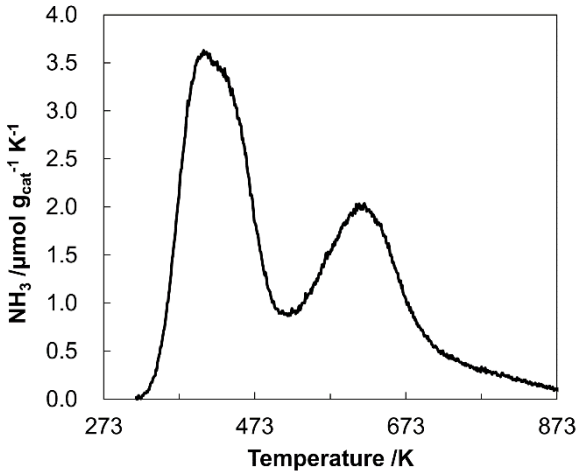


Fig. S3 NH_3-TPD profile for Hβ(75). Hβ(75) 53 mg, He 30 mL min^{-1}, 10 K min^{-1}. Acid amount (310 μmol g^{-1}) was calculated from the area of *h*-peak.

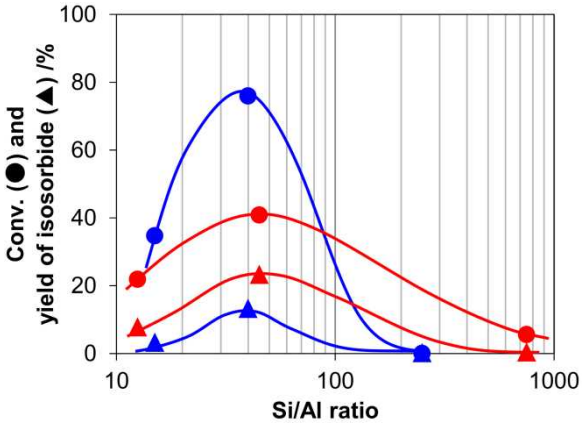


Fig. S4 Effects of Si/Al ratios of HUSY (blue) and HZSM-5 (red) on the dehydration of sorbitol at 400 K for 1 h.

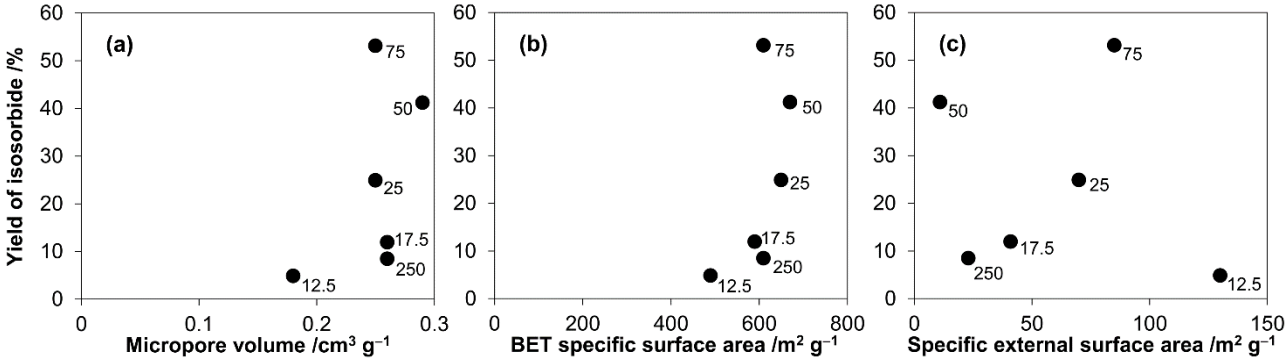


Fig. S5 Plots of isosorbide yield at 1 h against (a) micropore volume, (b) BET specific surface area and (c) external surface area for Hβ zeolites with varied Si/Al ratios. Values in graphs show Si/Al ratios. Hβ(50) is active regardless of the low external surface area. This result supports that the internal acids are major active sites.

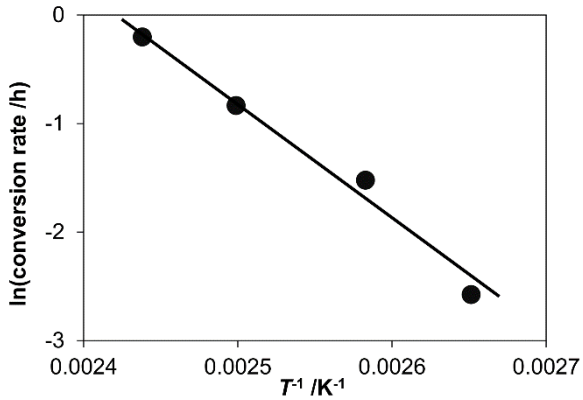


Fig. S6 Temperature dependence of the dehydration of sorbitol. Sorbitol 182 mg, Hβ(75) 10 mg.

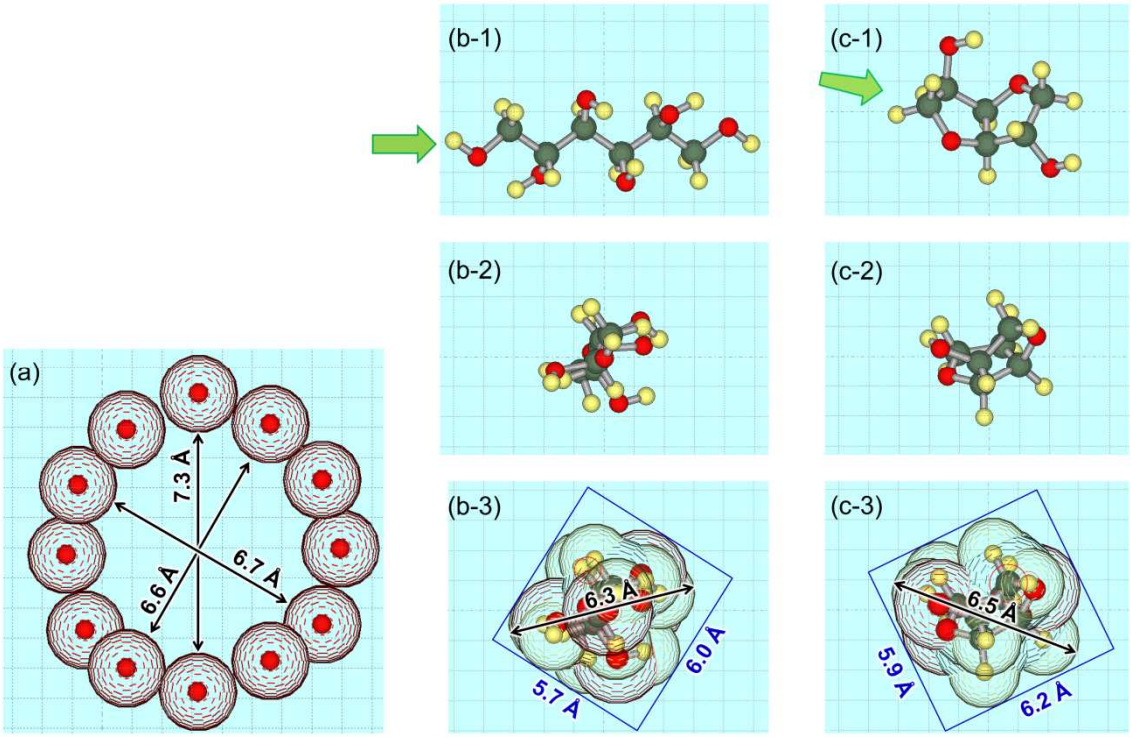


Fig. S7 Models of (a) oxygen twelve-membered ring of *BEA <100> (atomic positions were obtained from International Zeolite Association), (b) sorbitol and (c) isosorbide. For (b) and (c), (1) provides a typical view of the molecule, (2) shows the molecule viewed from the green-arrow direction, and (3) represents a space-filling model of (2). Space filling is based on ionic radius for *BEA and van der Waals radius for sorbitol and isosorbide. 1 mesh = 1 Å.

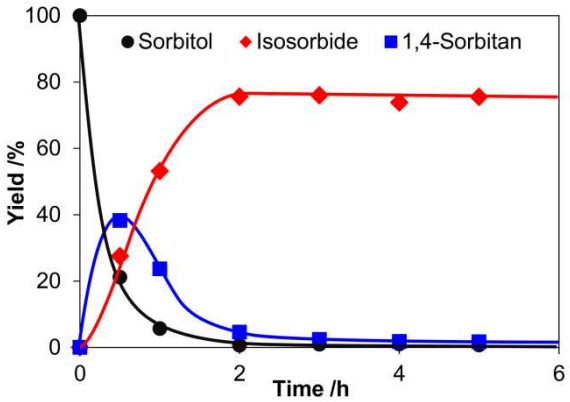


Fig. S8 Time course of sorbitol dehydration by Hβ(75) at 400 K.

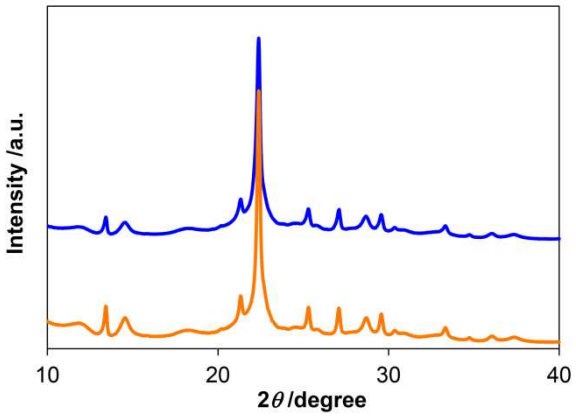


Fig. S9 XRD patterns of fresh Hβ(75) (orange) and that after reuse for 5 times (blue).

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