

## **Supporting Information**

### **Selective Dehydration of Mannitol to Isomannide over H-Beta Zeolite**

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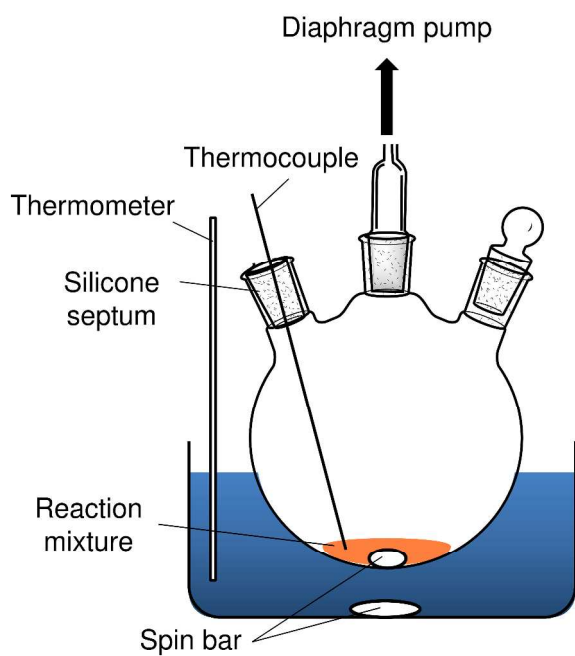
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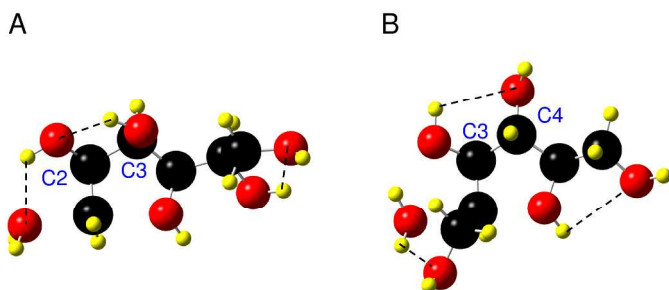
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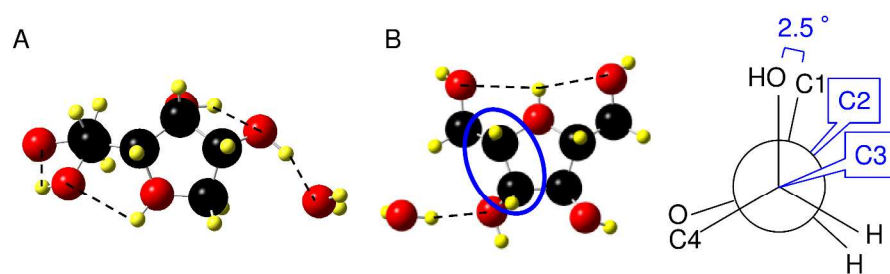
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**Figure S1.** Diagram of the reaction apparatus.

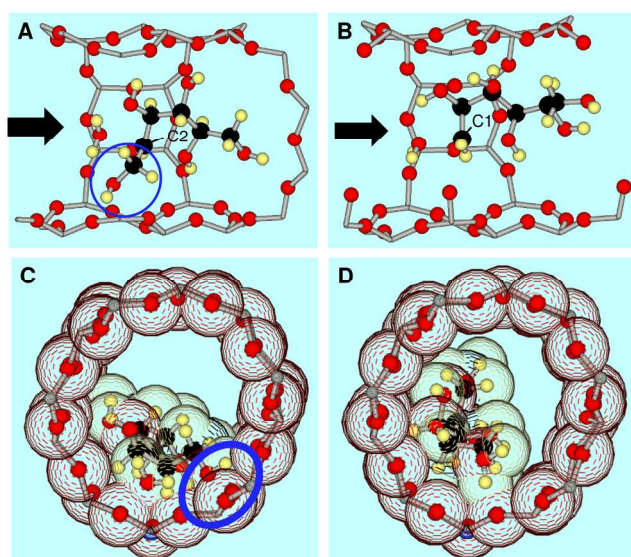


**Figure S2.** Transition states of (A) 1,4-dehydration and (B) 2,5-dehydration. Black lines show hydrogen bonds.

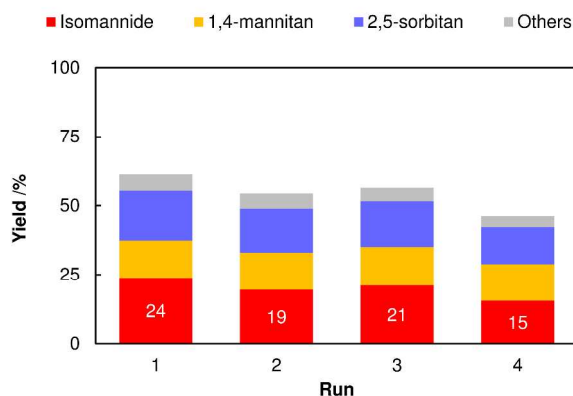


**Figure S3.** Configuration of products in (A) 1,4-dehydration and (B) 2,5-dehydration.

Black lines are hydrogen bonds and the blue circle shows the eclipsed conformation.



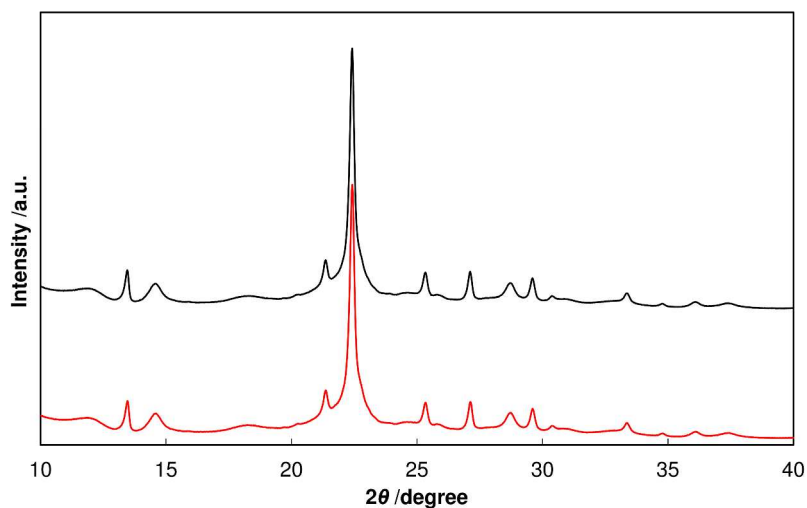
**Figure S4.** Transition states of (A) 2,5-dehydration and (B) 1,4-dehydration placed on a typical acid site in the \*BEA pore structure. C and D show the molecules viewed from the direction of the black arrows in A and B, which are illustrated as space-filling models using van der Waals radii. Black: carbon; red: oxygen; yellow: hydrogen; gray: silicon (shown in ionic radius); blue: aluminum (shown in ionic radius). The CH<sub>2</sub>OH group is sterically conflicted with the zeolite framework as highlighted by a blue circle.



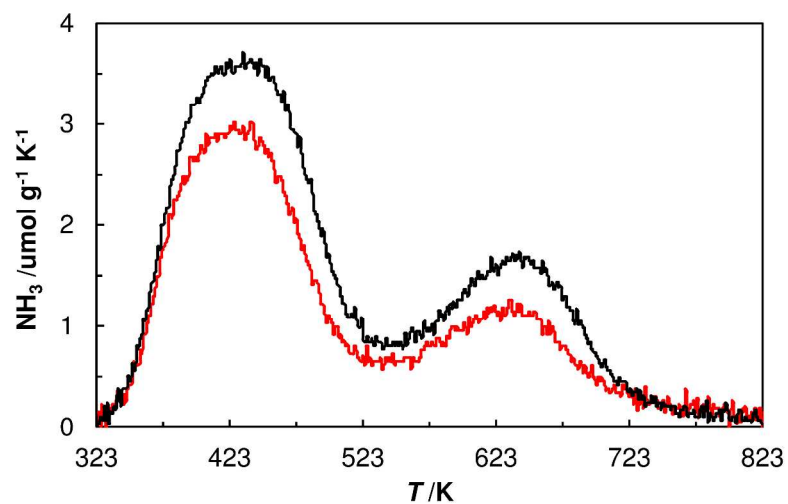
**Figure S5.** Reuse experiments of H $\beta$ (75) in the dehydration of mannitol at 423 K for 15 min.

Reuse experiments of H $\beta$ (75) were conducted at 423 K for 15 min to elucidate the durability by keeping the conversion level at 50–60% (Figure 5). The fresh catalyst gave 61% conversion and 24% yield of isomannide. After the reaction, the used catalyst turned brown in color due to coking. The BET surface area was decreased from 600 to 360 m<sup>2</sup> g<sup>-1</sup> and the total pore volume was also reduced from 0.25 to 0.13 cm<sup>3</sup> g<sup>-1</sup>. Next, the used catalyst was calcined to remove coke at 823 K for 8 h prior to the reuse experiment. Conversions of mannitol were 54%, 56%, and 46% in the reuse tests, which were lower than that given by the fresh catalyst. However, the selectivity toward 1,4-dehydration was maintained at 61–62%, which indicates that the catalyst is reusable by increasing the reaction time to obtain a similar yield of isomannide at 423 K. Intensities of the XRD diffraction peaks for the used catalyst were similar to the original catalyst (Figure S6), and the BET surface area was also similar to that of the original catalyst (600 and 590 m<sup>2</sup> g<sup>-1</sup> before and after the repeated reactions). Hence, structural changes after the repeated

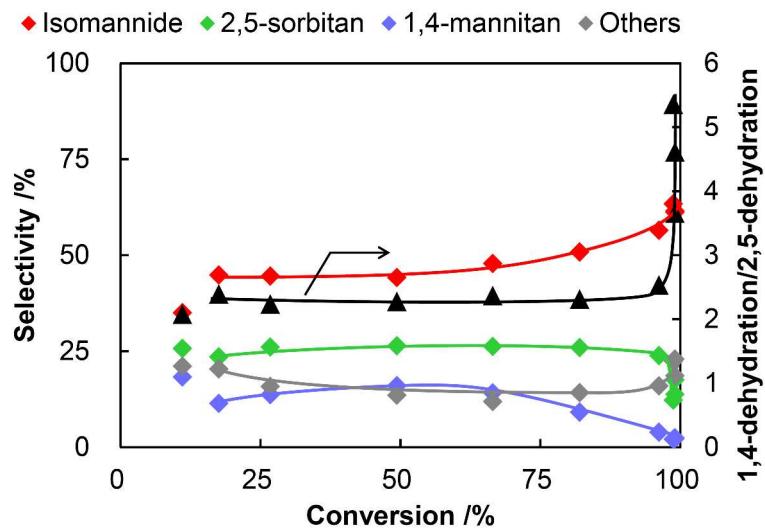
reactions were small, thus maintaining the selectivity in the reactions. However, the acid amount decreased from 0.22 to 0.17 mmol g<sup>-1</sup> as indicated by the NH<sub>3</sub>-TPD analysis in Figure S7, despite no change in the Si/Al ratio determined by EDX. This result implies the formation of extra-framework aluminum oxide during the reaction.



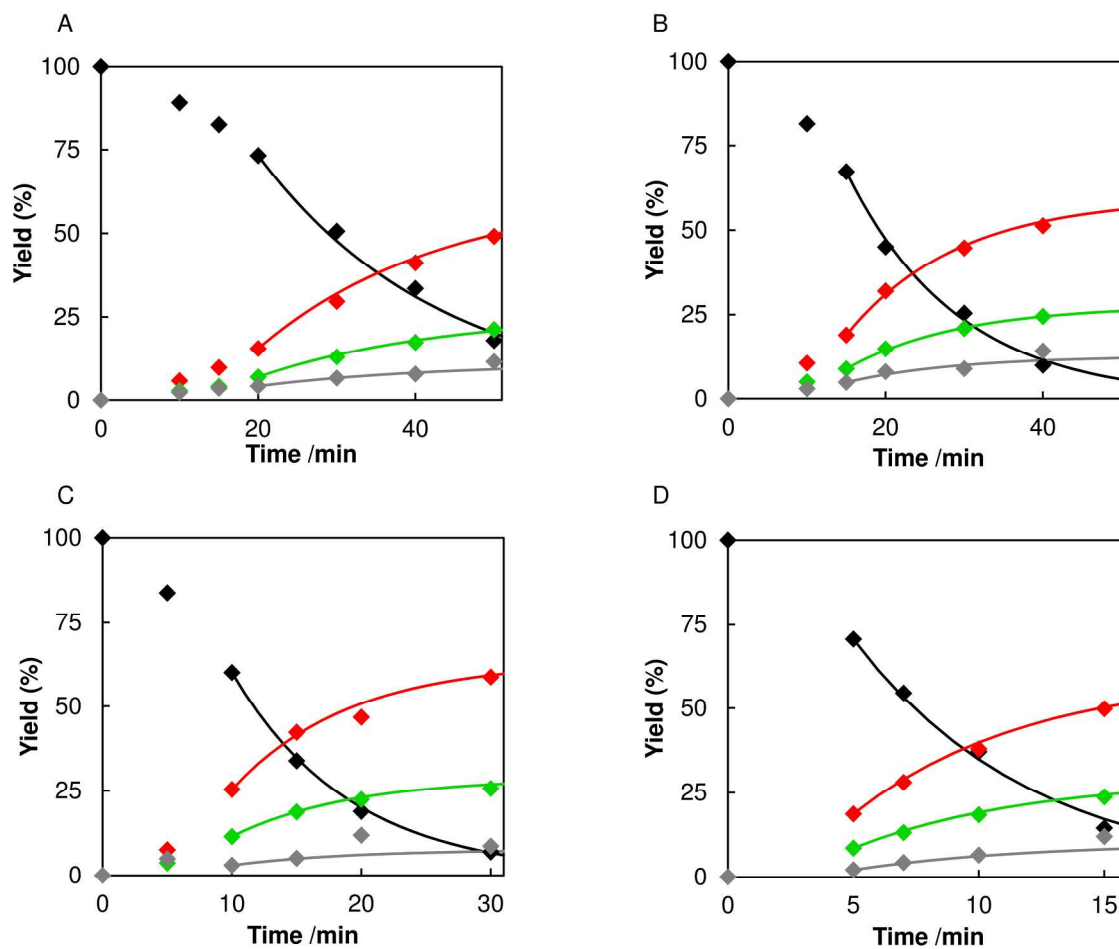
**Figure S6.** XRD patterns of fresh Hβ(75) (black) and after reuse 4 times (red).



**Figure S7.**  $\text{NH}_3$ -TPD profile for  $\text{H}\beta(75)$ .  $\text{He}$   $30 \text{ mL min}^{-1}$ ,  $10 \text{ K min}^{-1}$ . Black: Fresh catalyst 47 mg; red: catalyst after reuse 4 times, 44 mg.

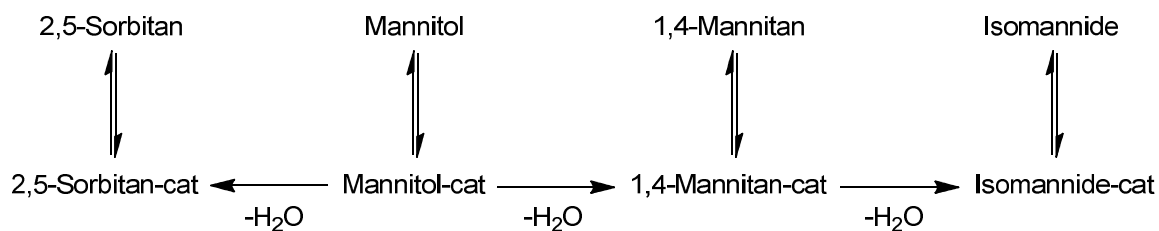


**Figure S8.** Selectivity of products against conversion at 413 K.



**Figure S9.** Time courses of mannitol dehydration over H $\beta$ (75) at (A) 413 K, (B) 418 K, (C) 423 K, (D) 428 K. Black: remaining mannitol; red: total yield of 1,4-mannitan and isomannide; green: 2,5-sorbitan; grey: unidentified products.





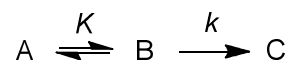
**Scheme S1.** Rake mechanism for the dehydration of mannitol over H $\beta$ . Formation pathways of by-products are omitted for simplicity.

**Table S1.** Gibbs free energy change ( $\Delta G$ ) in mannitol dehydration predicted by quantum calculation.

Reaction	B3LYP/6-31G(d)	MP2/6-311+G(2d,p)
1,4-Dehydration	-29 kJ/mol	-30 kJ/mol
2,5-Dehydration	-22 kJ/mol	-31 kJ/mol

## Equations

The rate of a reaction containing pre-equilibrium can be expressed as follows:



$$d[C]/dt = k[B]$$

When  $K \ll 1$ ,

$$\Leftrightarrow d[C]/dt = kK[A]$$

$\Leftrightarrow d[C]/dt = A \cdot \exp(-E_a/RT) \cdot \exp[-(\Delta H^\circ - T\Delta S^\circ)/RT] \cdot [A]$ , where  $A$  and  $E_a$  are the frequency factor and the activation energy in an elementary step ( $B \rightarrow C$ ), and  $\Delta H^\circ$  and  $\Delta S^\circ$  are standard enthalpy and entropy changes in the pre-equilibrium ( $A \rightleftharpoons B$ ).

$$\Leftrightarrow d[C]/dt = A \cdot \exp(\Delta S^\circ/R) \cdot \exp[-(E_a + \Delta H^\circ)/RT] \cdot [A]$$

Thus, the apparent activation energy is  $(E_a + \Delta H^\circ)$ . This is for the 1,4-dehydration, where  $\Delta H^\circ > 0$ .

When  $K \gg 1$ , the apparent activation energy becomes  $E_a$ . This is for the 2,5-dehydration.