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Dehydration of sorbitol to isosorbide over H-beta zeolites with high Si/Al ratios†

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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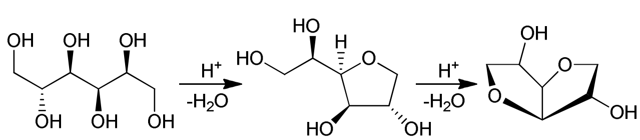
Conversion of sorbitol to isosorbide by heterogeneous catalysts is a challenge in biorefinery. Herein, H-beta zeolites with specific Si/Al ratios uniquely give isosorbide in up to 76% yield under mild conditions. Mechanistic study has suggested that acid sites on hydrophobic internal surface are active for this reaction.

Catalytic transformation of cellulosic biomass to chemicals is a crucial technology in the biorefinery for pursuing sustainability.[1] The hydrolytic hydrogenation of cellulose gives sorbitol in up to 90% yield,[2] and cellulose in real biomass has also been successfully converted to sorbitol.[3] Sorbitol is one of the top-ten platform chemicals in biorefinery proposed by US Department of Energy,[4] and the most promising derivative of sorbitol is isosorbide (Scheme 1).[1d,5] Isosorbide polycarbonate, commercialised as DURABIO® and PLANEXT®, is an engineering plastic with superior characteristics of both polymethyl methacrylate and bisphenol-A polycarbonate. Incorporation of isosorbide units into polyethylene terephthalate is a solution for high-temperature applications such as hot-beverage containers. Dimethyl isosorbide is a low-toxic and high-boiling solvent (b.p. 509 K).[6] Besides, isosorbide diesters are plasticisers for the production of flexible polyvinyl chloride. Isosorbide nitrates are medicines for angina pectoris, and isosorbide itself is used for treating glaucoma, brain hypertension and Ménière's disease.



Scheme 1 Dehydration of sorbitol to isosorbide.

The conversion of sorbitol to isosorbide (Scheme 1) has required liquid sulphuric acid as a catalyst in industry, which provides good yields of isosorbide (70–77%) at *ca.* 400 K within a few hours in batch reactors.[7,8] Major obstacles of this system are difficult separation of isosorbide from the reaction mixture and discharge of a large amount of sulphuric acid pitch.[9] Thus, solid acid catalysts such as zeolites,[8,10] mixed oxides,[11] phosphated or sulphated oxides,[10d,12] sulphonic resins[13] and Ru–Cu bimetals[14] have been investigated to replace the homogeneous acid. Additionally, hot compressed water was applied to the synthesis of isosorbide.[15] Among them, zeolites would be prospective choices for the dehydration of sorbitol, as they are composed of ubiquitous elements (Si, Al, O) with thermal stability and tunable properties. However, zeolites tested in previous reports have shown low activities and required severe reaction conditions. For example, an H-beta with a Si/Al ratio of 12.5, denoted Hβ(12.5), gave only a 38% yield of isosorbide in the dehydration reaction at 423 K for 12 h.[8] HZSM-5(40) produced isosorbide in 59% yield at 533 K over 14 h.[10b] Thus, it is necessary to explore zeolite catalysts working under mild conditions similar to those for sulphuric acid. Herein, we report that raising Si/Al ratio of Hβ to 75 drastically improves the activity, giving isosorbide in 76% yield at 400 K within 2 h.

Dehydration of sorbitol was conducted at 400 K for 2 h in the presence of various zeolites with similar Si/Al ratios (Table 1) in a Pyrex flask (Fig. S1, ESI†). Hβ(50) produced isosorbide in 72% yield with >99% conversion of sorbitol (entry 2), which was in contrast to the low activity of Hβ(12.5) reported previously (38% yield even at 423 K for 12 h).[8] An intermediate for the formation of isosorbide, 1,4-sorbitan, was yielded in 4.5%. Other identified products were 2,5-mannitan (3.1%) and 2,5-iditan (Scheme S1, ESI†). 2,5-Iditan and a monoanhydrohexitol (*AH*) other than 3,6-sorbitan were overlapped in our HPLC analysis (Fig. S2, ESI†), and their total yield was 9.2%. Hβ(50) became brownish after the reaction due to slight coking, but it can be regenerated by calcination (see below). HUSY(40) provided a high conversion of 97% but the yield of isosorbide was as low as 28%, which was due to the formation of large amounts of by-products (40%; entry 3). HZSM-5(45) and HMOR(45) were also less active than Hβ(50) (isosorbide yield: 27% and 2.3%, respectively; entries 4 and 5). Hβ was uniquely active and selective for the formation of isosorbide among the zeolite catalysts tested. The good activity of Hβ may be due to the twelve-membered-ring and three-dimensional porous structure with no excess space (supercage) causing side-reactions,

Table 1 Dehydration of sorbitol by zeolite catalysts[a]

Entry	Catalyst	Reaction time /h	Conv. /%	Yield of product /%		Yield of by-product /%		
				Isosorbide	1,4-Sorbitan	2,5-Mannitan	2,5-Iditan and *AH*[b]	Others[c]
1	None	2	<1	0.0	0.0	0.0	0.0	<1
2	Hβ(50)	2	>99	73	4.5	3.1	9.2	10
3	HUSY(40)	2	97	28	29	10	20	10
4	HZSM-5(45)	2	51	27	7.1	1.0	0.9	15
5	HMOR(45)	2	18	2.3	11	0.9	2.6	1
6	Hβ(75)	2	>99	76	4.6	2.9	5.9	10
7	Hβ(75)	1	94	53	24	2.7	6.5	8
8	Hβ(75)[d]	1	96	58	19	2.8	6.9	9
9	Hb(75)[e]	1	96	56	22	2.7	6.8	9

[a] Sorbitol 182 mg (1.00 mmol), catalyst 50 mg, 400 K. [b] *AH*: a monoanhydrohexitol other than 3,6-sorbitan. [c] (Conversion) – (Total yield of shown products). [d] Modified with triphenylsilane. [e] 2,4,6-Tri-*tert*-butylpyridine (5 mg) was added.

whereas acid strength[16] is a minor factor in this case. The detailed discussion is available in ESI†.

The use of Hβ(50) instead of Hβ(12.5)[8] remarkably improved the reaction performance as described above, which prompted us to study the effect of Si/Al ratio on dehydration activity of Hβ. Fig. 1 represents the correlation between the Si/Al ratios of Hβ and the results of the dehydration of sorbitol at 400 K for 1 h. Yield of isosorbide and conversion of sorbitol were maximised at Si/Al = 75, and both decreasing and increasing the Si/Al ratio declined the activity. It is noteworthy that Hβ(75) provided the highest yield of isosorbide (76%) at a longer reaction time of 2 h (Table 1, entry 6). Turnover number for the dehydration was 100, based on the quantity of acid sites [16 μmol in 50 mg Hβ(75), determined by NH_3-temperature programmed desorption; Fig. S3, ESI†]. In addition, HUSY and HZSM-5 also provided volcano-type dependence (Fig. S4, ESI†). We assume that both acid site and hydrophobicity are necessary for good catalytic performance. In general, increase of Si/Al improves hydrophobicity, which thermodynamically enhances the removal of water molecules formed in the dehydration of sorbitol. It is known that hydrophobic zeolites can function as acid catalysts even in aqueous phase.[17] At the same time, raising the Si/Al ratio reduces the number of acid site, which is roughly equal to the content of Al in these cases.[18] In contrast to acid amount, acid strength is a minor factor, since this parameter is independent of Si/Al ratio for high-silica zeolites as used in this study.[18] Effect of porosity is also minor in this comparison, as the Hβ zeolites have similar micropore volumes (0.25–0.29 cm^3 g^{-1}) and specific surface areas (590–670 m^2 g^{-1}) except for Hβ(12.5) (Table S1, Fig. S5a,b, ESI†). In addition, external surface area has no influence on the activity (Table S1, Fig. S5c, ESI†), because internal acids work for the reaction as described below. Hence, the

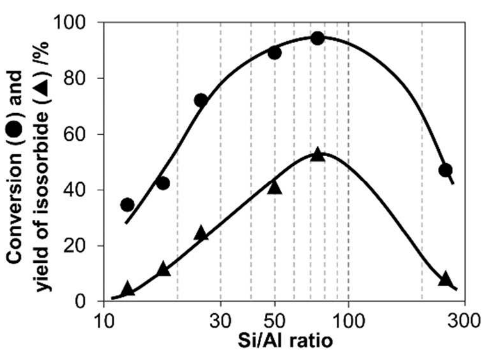


Fig. 1 Effect of Si/Al ratio of Hβ on the dehydration of sorbitol at 400 K for 1 h.

volcano-type curve can be depicted for the catalytic activity against Si/Al ratio, and the best catalyst, Hβ(75), has been used for the further study.

Active sites of Hβ(75) on external or internal surfaces were estimated by selectively blocking external ones. First, external surface of Hβ(75) was covered with triphenylsilane;[19] however, pristine and the modified Hβ(75) provided similar catalytic activity in the dehydration of sorbitol for 1 h (isosorbide yield: 53% and 58%, respectively; Table 1, entries 7 and 8). Second, we conducted the dehydration of sorbitol over Hβ(75) in the presence of 2,4,6-tri-*tert*-butylpyridine in order to poison external acid sites,[20] but a similar isosorbide yield was obtained (56%, entry 9). Hence, the activity is not ascribed to external acid sites but internal ones. Besides, the apparent activation energy determined by an initial rate method was 89 kJ mol^{-1} for Hβ(75) (Fig. S6, ESI†), which was not in the range of diffusion[21] but of chemical reactions (dehydration). Since pore size of *BEA (6.6×6.7 Å) is larger than the cross-sections of sorbitol (5.7×5.9 Å) and isosorbide (5.9×6.2 Å) (Fig. S7, ESI†), quick diffusion of these molecules are possible in the pores. Davis *et al.* also have revealed that the rate-determining step of a sugar conversion (isomerisation of glucose) over β zeolite is a chemical reaction (hydride shift).[22] Accordingly, it is concluded that the predominant active sites are internal acids, which is a cause of the obvious dependence of catalytic activity on pore structures of zeolites. This fact also supports the importance of hydrophobicity; water molecules produced by the reaction can be strongly adsorbed in pores due to the small diameter, and therefore we tentatively propose that water needs to be destabilized by hydrophobic nature for the desorption.

Finally, reuse experiments of Hβ(75) were conducted to evaluate the durability in the dehydration of sorbitol at 400 K for 2 h, as fresh Hβ(75) required 2 h for completing the reaction (Fig. S8, ESI†). The first reaction gave an isosorbide yield of 76%, but the used catalyst afforded a decreased yield (67%) of isosorbide. Coking (carbon 9.2 wt%) was found in the used catalyst, and it decreased Brunauer-Emmett-Teller (BET) specific surface area from 610 to 260 m^2 g^{-1} and micropore volume from 0.25 to 0.11 cm^3 g^{-1}. Then, the used catalyst was calcined at 823 K for 8 h, by which the surface area and the micropore volume were returned to 640 m^2 g^{-1} and 0.27 cm^3 g^{-1}, respectively. Al content was maintained after the calcination. Using this reactivation method, the yields of isosorbide were 76%, 75%, 73%, 72% and 65% in repeated five runs (Fig. 2). The catalytic activity is largely recovered by the removal of coke, and the remaining small decline in the yield would be compensated by increasing reaction time or temperature. Since X-ray diffraction peaks of *BEA was slightly weakened (Fig.

S9, ESI†), partial degradation of the crystals probably reduces the catalytic activity. This assumption agrees well with a fact that the good catalytic activity is provided by *BEA structure.

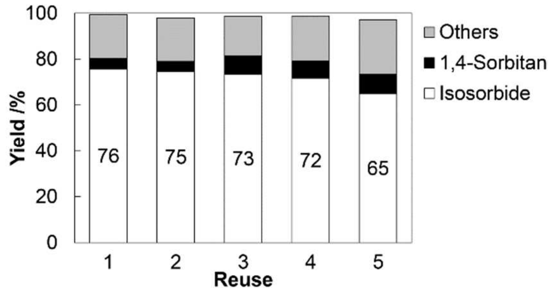


Fig. 2 Reuse experiments of Hβ(75) in the dehydration of sorbitol at 400 K for 2 h.

Conclusions

Hβ is the most active catalyst for the dehydration of sorbitol among zeolites tested. Optimisation of Si/Al ratio unexpectedly raises the catalytic activity, and Hβ(75) achieved the highest isosorbide yield of 76%. It is proposed that acidic sites on internal surface of Hβ with hydrophobic natures are active for this reaction.

Acknowledgements

This work was supported by a Grant-in-Aid for Young Scientists (26709060) from Japan Society for the Promotion of Science (JSPS).

Notes and references

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