Supporting information

Selective Dehydration of Sorbitol to 1,4-anhydro-D-sorbitol Catalyzed by Polymer-supported Acid Catalyst

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Table 1S. The composition of the polymer catalysts.

Entry	Catalysts	C%[a]	H%[a]	N%[a]	S%[b]	Si%[b]
1	SO_3H-PS-SO_3H	35.8(34.2)	5.4(5.5)	6.7(6.8)	11.4(11.2)	5.0(5.1)
2	SO_3H-PS-SO_3H[c]	35.7	5.4	6.7	11.3	5.0
3	0.3SO_3H-PS-0.3SO_3H	43.9(42.7)	7.3(7.5)	5.6(5.4)	4.4(4.6)	8.6(8.7)
4	0.6SO_3H-PS-0.6SO_3H	43.0(43.5)	6.6(6.5)	5.6(5.7)	7.2(7.3)	7.1(7.0)
5	2SO_3H-PS-2SO_3H	41.2(40.8)	5.4(5.3)	5.7(5.7)	12.9(13.1)	3.8(3.7)
6	3SO_3H-PS-3SO_3H	40.4(40.6)	5.1(5.4)	5.6(5.8)	14.5(14.1)	2.9(2.8)
7	SO_3H-PS	39.1(39.5)	5.5(5.3)	5.4(5.5)	10.8(11.1)	5.6(5.6)
8	SO_3H-PS[c]	40.1	5.5	5.4	6.4	5.8
9	PS-SO_3H	31.6(32.2)	5.5(5.5)	9.2(9.4)	10.7(10.9)	4.8(4.7)
10	PS-SO_3H[c]	32.6	5.6	10.2	6.4	4.9

[a]Determined by elemental analysis, [b]Determined by ICP-AES, [c] The catalyst was recycled five times in sorbitol dehydration. The values in the parathesis refer to calculated results.

Table 2S The BET surface area of various catalysts.

Catalysts	BET surface areas ($m^2 \bullet g^{-1}$)
SO_3H-PS-SO_3H	29.47
0.3SO_3H-PS-0.3SO_3H	25.81
0.6SO_3H-PS-0.6SO_3H	27.49
2SO_3H-PS-2SO_3H	35.42
3SO_3H-PS-3SO_3H	42.85
SO_3H-PS	28.48
PS-SO_3H	28.36
Amberlyst-15	45

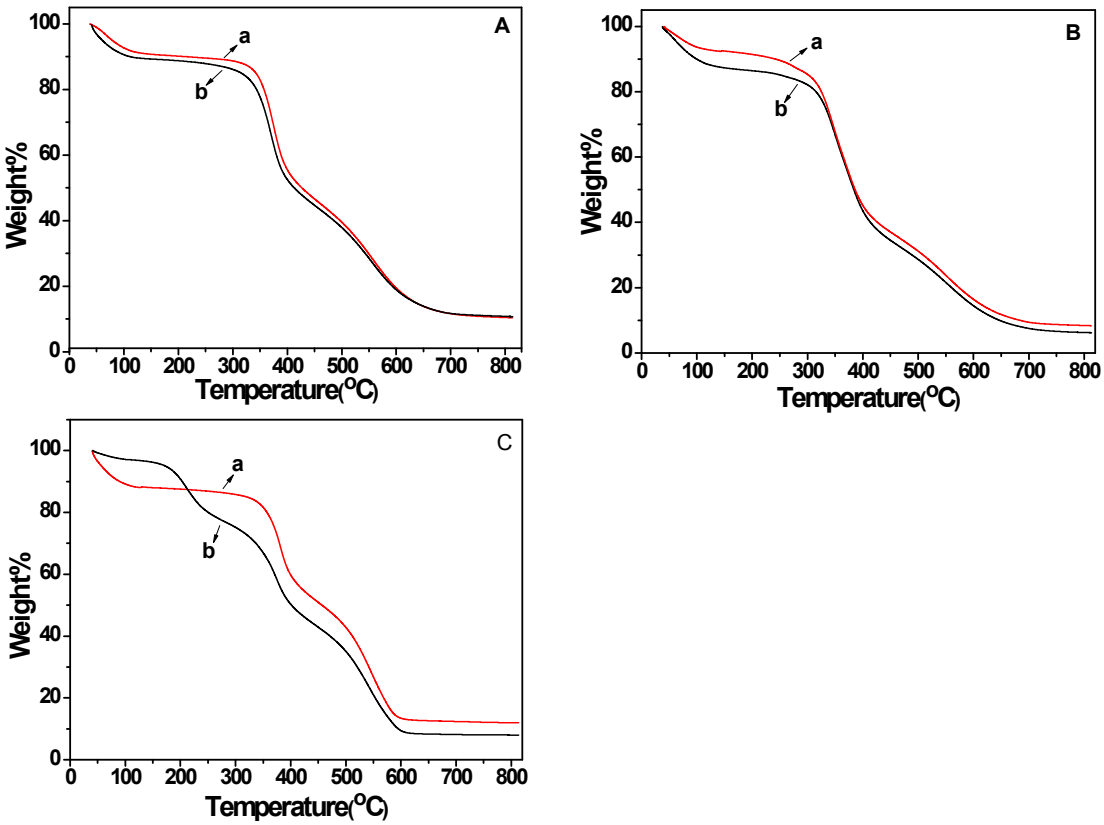


Fig. 1S Thermogravimetric analysis (TGA) curves of polymer-based catalysts. A) SO_3H-P-SO_3H, (B) P-SO_3H and (C) SO_3H-P. Curve (a) represented fresh catalyst and curve (b) the catalysts after the fifth runs.

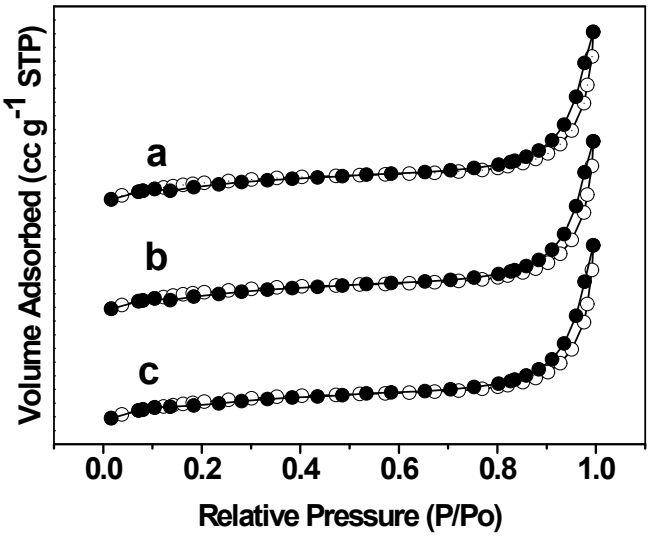


Fig. 2S N_2 sorption isotherms of a) PS-SO_3H, b) SO_3H-PS and c) SO_3H-PS-SO_3H.

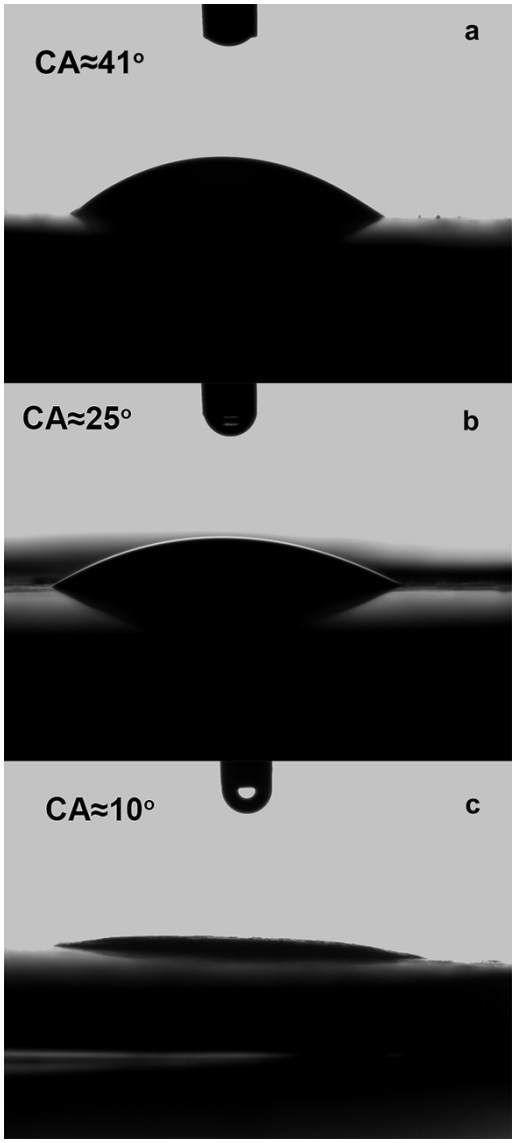


Fig. 3S Water contact angle over a) PS-SO_3H, b) SO_3H-PS and c) SO_3H-PS-SO_3H. catalyst.

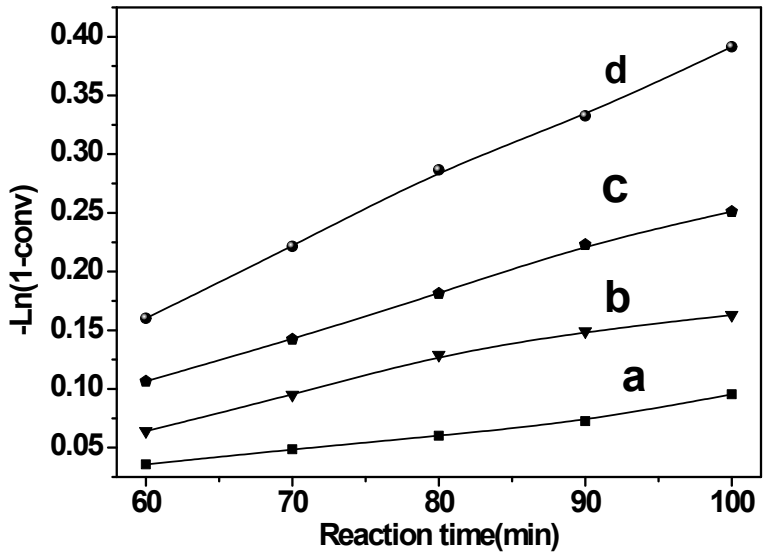


Fig. 4S Time courses of sorbitol dehydration in solvent free systerm using SO_3H-PS-SO_3H at various temperatures. (a) 120 ^oC, (b) 130 ^oC, (c) 140 ^oC, (d) 150 ^oC. Reaction condition: sorbitol (1.65 mmol), catalyst: SO_3H-PS-SO_3H (acid amounts: 0.27 mmol).

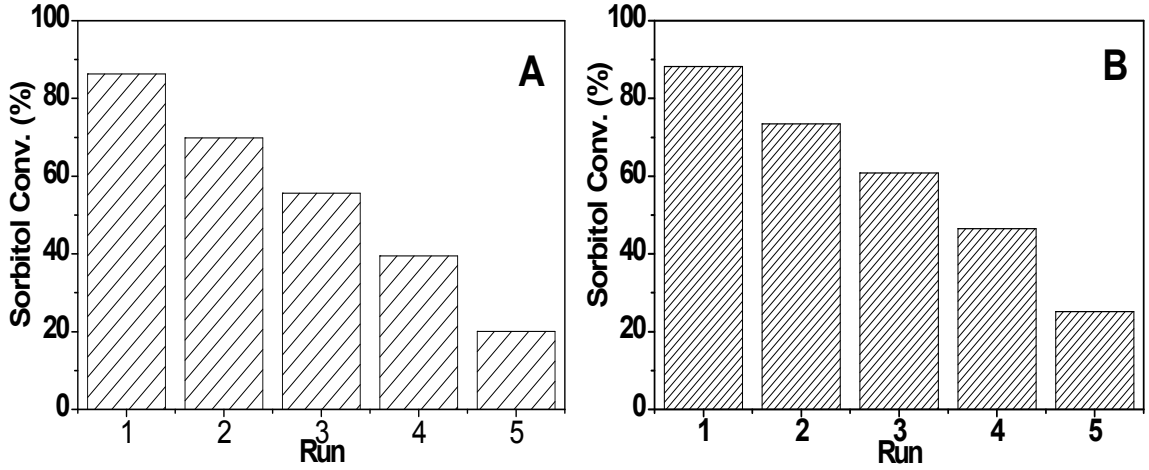
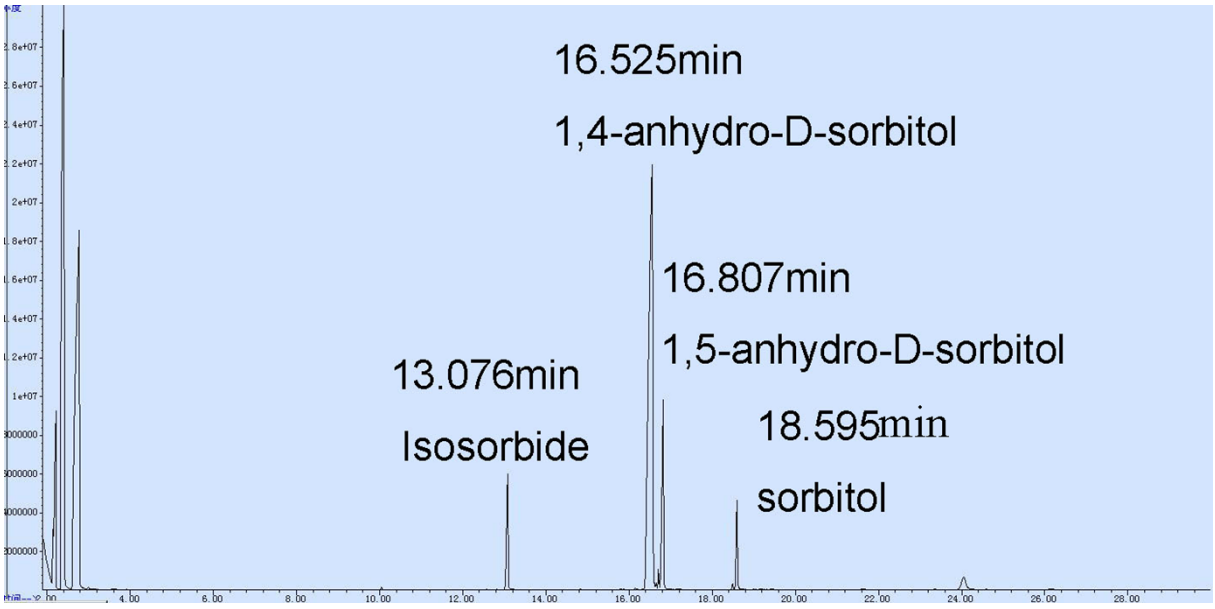


Fig. 5S Recyclability of the catalysts in sorbitol dehydration. A) PS-SO_3H and B) SO_3H-PS. Reaction condition: 150 ^oC, 4 h, 1.65 mmol sorbitol, 0.27 mmol catalyst. The selectivity of 1,4-anhydro-D-sorbitol are both more than 90%.

Derivatization of sorbitol dehydration products for GC-MS

Derivatization of sorbitol dehydration products was performed in a 25 mL round-bottomed with single neck flask. 0.5 g sorbitol products was introduced into the flask. Subsequently, 1 ml anhydrous pyridine and 1 ml acetic anhydride were added into single-neck flask. Then, the reactor was heated to 90 °C for 20 min. After the reaction, the reactor was cooled to room temperature. The derivatives products were analyzed by GC-MS [Agilent 6890/5973 GC-MS equipped with the HP-5MS column (30 m × 0.25 mm × 0.25 mm)].



Retention time/min

Fig. 6S GC-MS spectrum for an acetylated mixture obtained from sorbitol dehydration (433 K, 4 h)

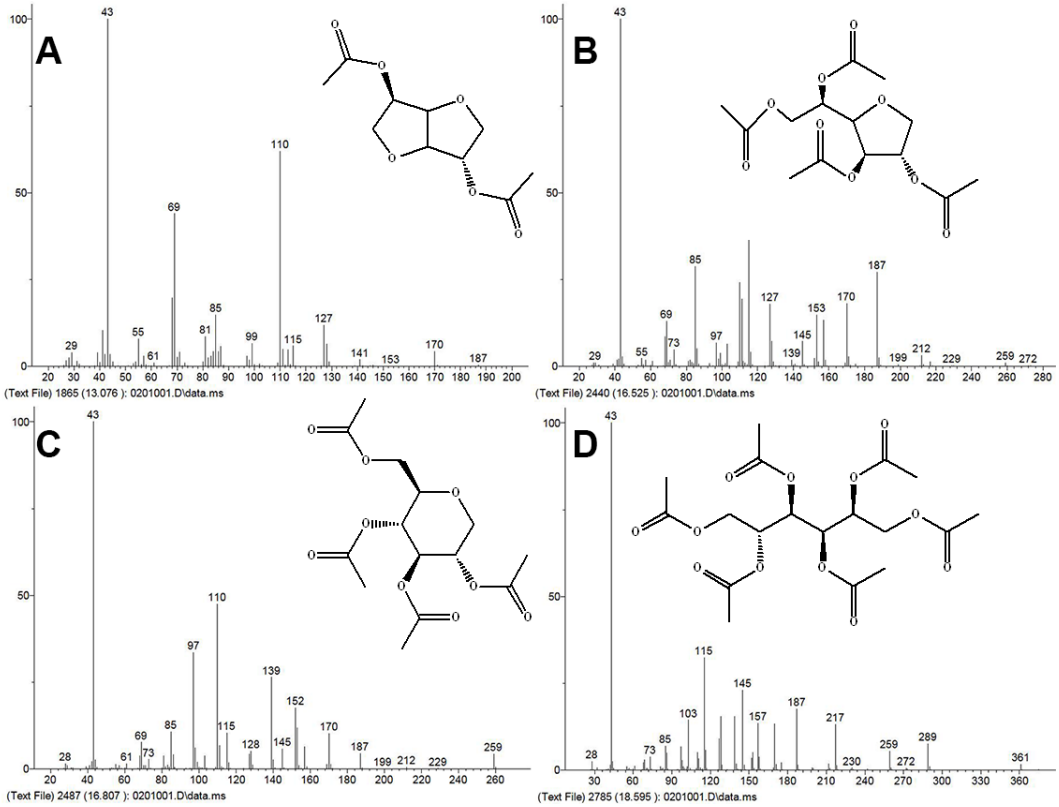


Fig. 7S MS spectra for A) acetylated isosorbide, B) acetylated 1,4-anhydro-D-sorbitol, C) acetylated 1,5-anhydro-D-sorbitol and D)acetylated sorbitol obtained from sorbitol dehydration.