Electronic supplemental information (ESI) for

PVP-stabilized heteropolyacids as reusable self-assembling catalysts for alcoholysis of cellulosic saccharides

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Table S1 The leached amount of PVP-HPAs during catalyzing the butanolysis of cellobiose[(a)]

Recycling number	Leached amount (wt%)	
	PVP-HPW (1/5:1)	PVP-HSiW (1/5:3/4)
1	10.6	5.3
2	2.0	1.3
3	0.9	1.1

(a) Detecting condition: After each time of recycling, the solution is separated by centrifugation; a certain column of solution is evaporated and is oxidized by nitrohydrochloric acid to remove the residue of organic compounds, then is diluted to a proposed concentration. The leached amount of PVP-HPAs is calculated based on the amount of W-element detected by ICP-OES.

Table S2 The results about catalyzed butanolysis and hydrolysis of cellobiose by HPAs and PVP-HPAs at low conversion[(a)]

Butanolysis of cellobiose						
Entry	Catalyst	Conversion (%)	Selectivity (%)			TOF (h^{-1})[(b)]
			TRS	β-BGS	α-BGS	
1	HPW	40.4	10.9	29.4	59.7	5.9
2	HSiW	38.4	10.2	29.4	60.4	5.6
3	PVP-HPW (1/5:1)	30.5	11.3	29.4	59.3	4.5
4	PVP-HSiW (1/5:3/4)	31.2	10.2	29.7	60.1	4.6
Hydrolysis of cellobiose						
Entry	Catalyst	Conversion (%)	Selectivity (%)			TOF (h^{-1})
			Glucose	Fructose		
5	PVP-HPW (1/5:1)	45.0	95.0	4.2		6.6
6	PVP-HSiW (1/5:3/4)	44.4	94.5	4.5		6.5

(a) The reaction condition is the same to that in the Table 1, but the reaction time is only 1 h and in the hydrolysis reaction the butanol is replaced by deionized water of 20 mL column. (b) Turnover frequency (TOF) means that per proton catalyzes the number of cellobiose molecular in 1 h.

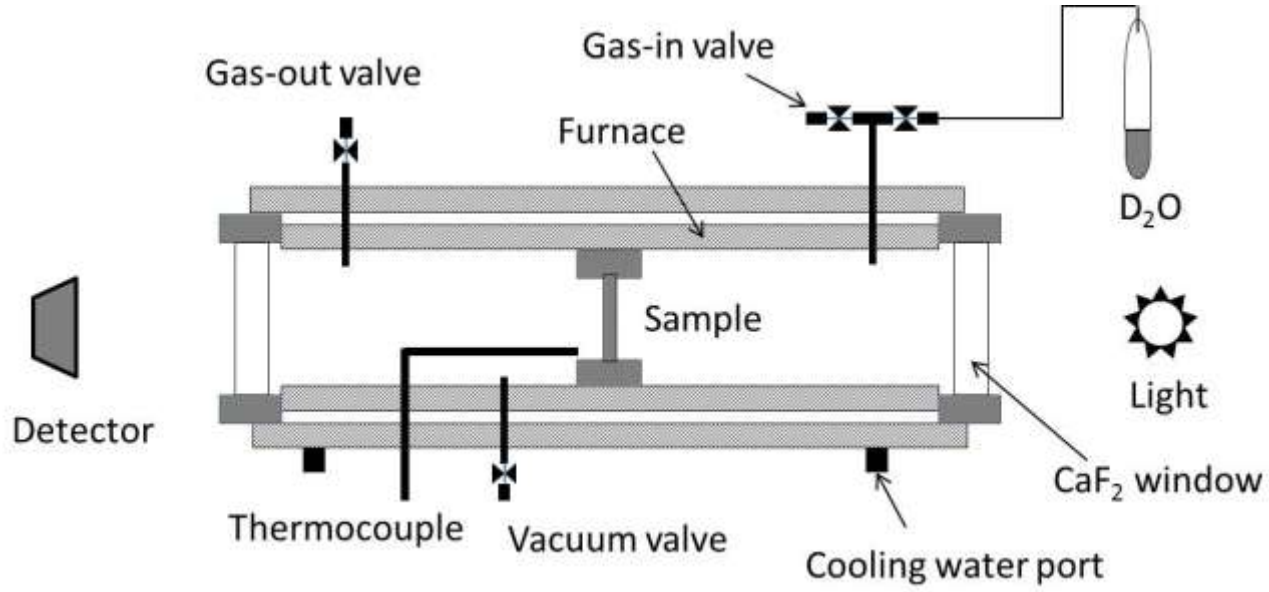

Fig. S1 Schematic drawing the structure of in-situ cell for H-D isotopic exchange.

The detail procedures include these: Firstly, the sample powder was dispersed in D_2O under ultrasound for 2h. Then, the slurry was drop onto a thin glass sheet measuring 10 mm×10 mm×0.15 mm and D_2O was vapored under infrared lamp to make a thin film on the glass sheet. Thirdly, after fixing the sample at a special holder the sample was loaded into the in-situ cell and the cell was sealed by CaF_2 widow. Fourthly, the sample was heated to 373 K under vacuum until the pressure inside was below 3 Pa. Fifthly, close the vacuum valve, open the valve linking the bottle containing D_2O and the sample stood up in the D_2O stream for 30 min; repeat the fourth and fifth procedure three times for insurance that proton was deuterated fully. Finally, the cell was cooled to 283 K under vacuum and the FTIR test was taken at the wavenumber range between 4000 and 2100 cm^{-1}. After deuteration, the samples are named as DPW, DSiW, PVP-DPW (1/5:1) and PVP-DSiW (1/5:3/4).

There are several tips for the measurement: (1) Because it is rather difficult to take a very thin self-supported sheet of sample for measurement, there is a need to choose a proper plate supporting the thin film; glass is transparent at the wavenumber range between 4000 and 2100 cm^{-1} and according to published paper the band assigned to D_2O is about 2500 cm^{-1}, thus the thin glass sheet is chosen. (2) The FTIR instrument and in-situ cell were put in a plastic box filled with N_2 for eliminating interference from the CO_2 in air, because the two bands assigned to CO_2 are at about 2400 cm^{-1}. However, when the in-situ cell was transferred from the outside air into the box, because of the low temperature of the cell outside, the water in air was liquefied on the window; as a result, there is a broad band at 3200 cm^{-1} assigned to the water.

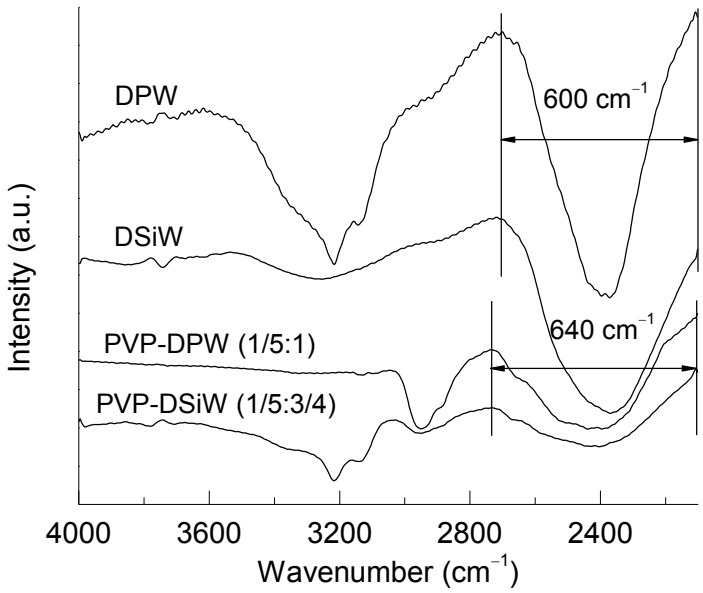

Fig. S2 The results of FTIR in H-D isotropic exchange.

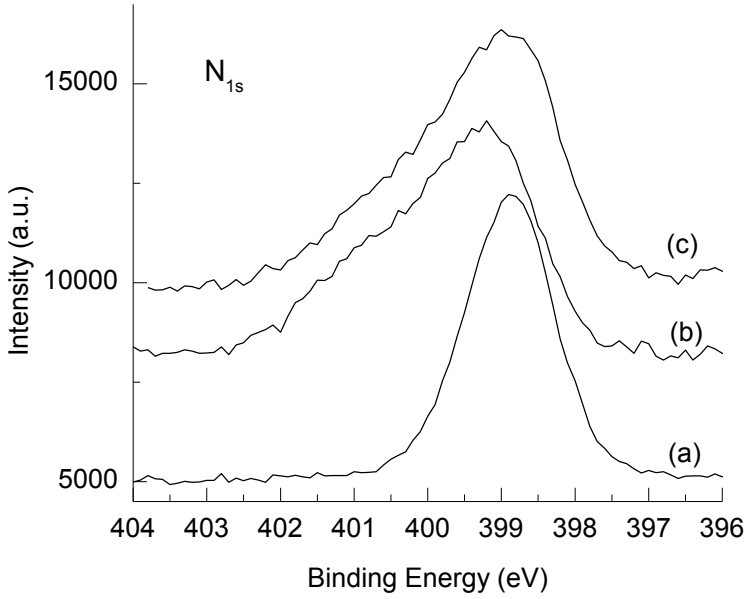

Fig. S3 XPS results of N1s (a) PVP, (b) PVP-HPW (1/5:1), and (c) PVP-HSiW (1/5:3/4).

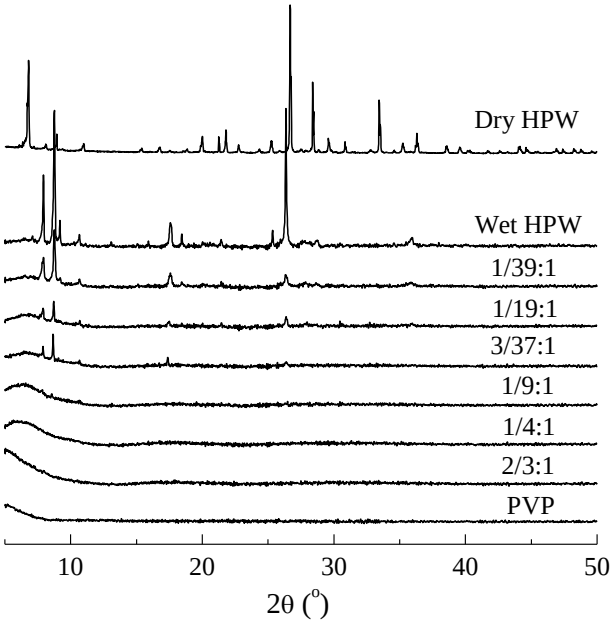

Fig. S4 The results of XRD patterns.

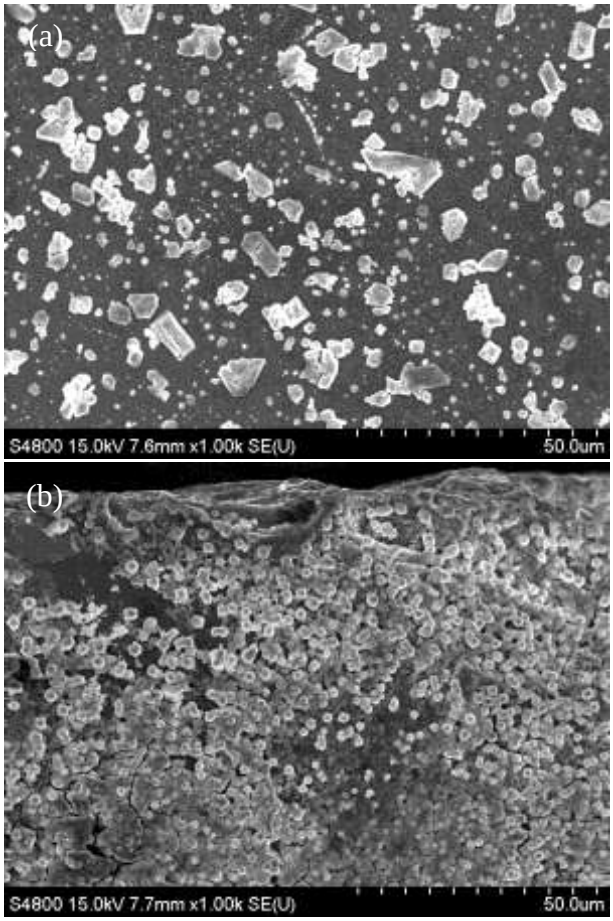

Fig. S5 (a) The SEM image of HPW. (b) The SEM image of PVP-HPW (1/5:1).

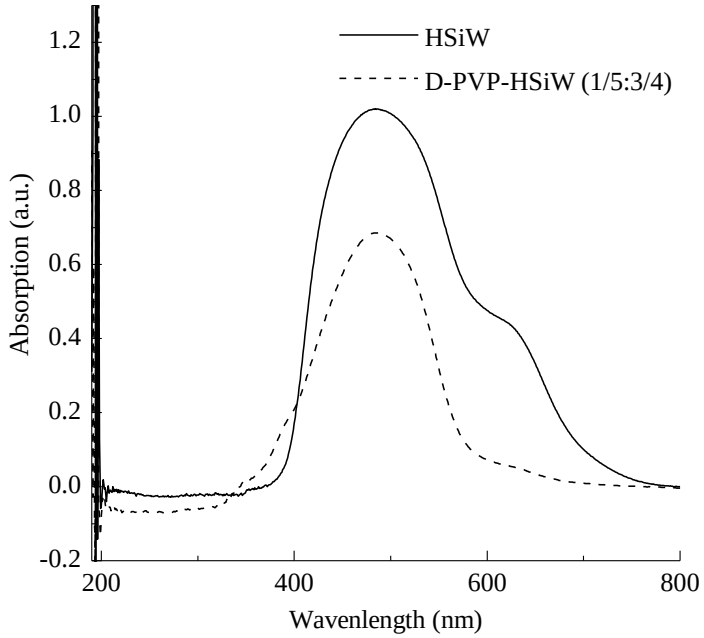

Fig. S6 Results of DSR Uv-Vis

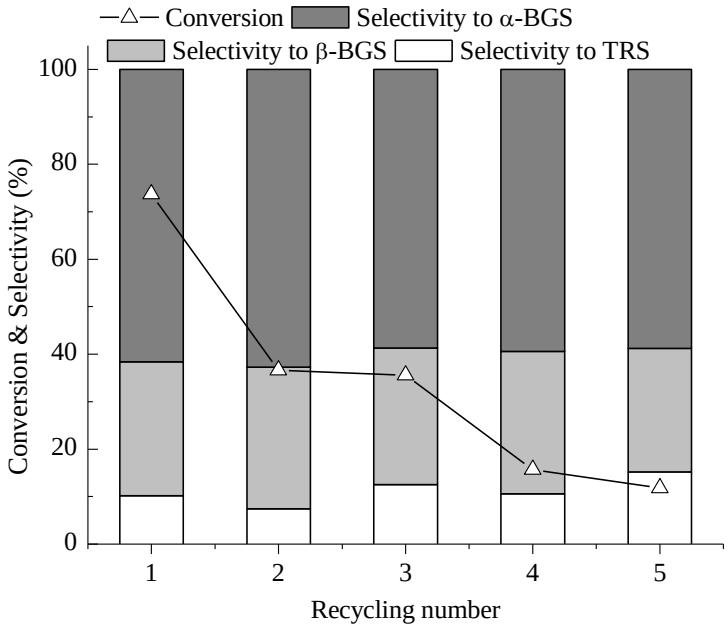

Fig. S7 Recycling performance of PVP-HPW (1/5:1) in catalyzed butanolysis of cellulose. The reaction condition is the same to that in Table 1.

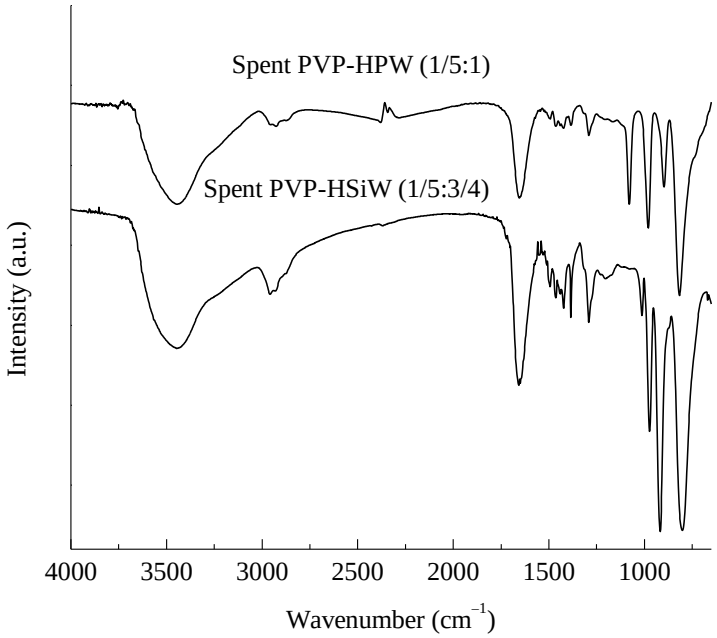

Fig. S8 FTIR spectra of spent PVP-HPW (1/5:1) and PVP-HSiW (1/5:3/4).

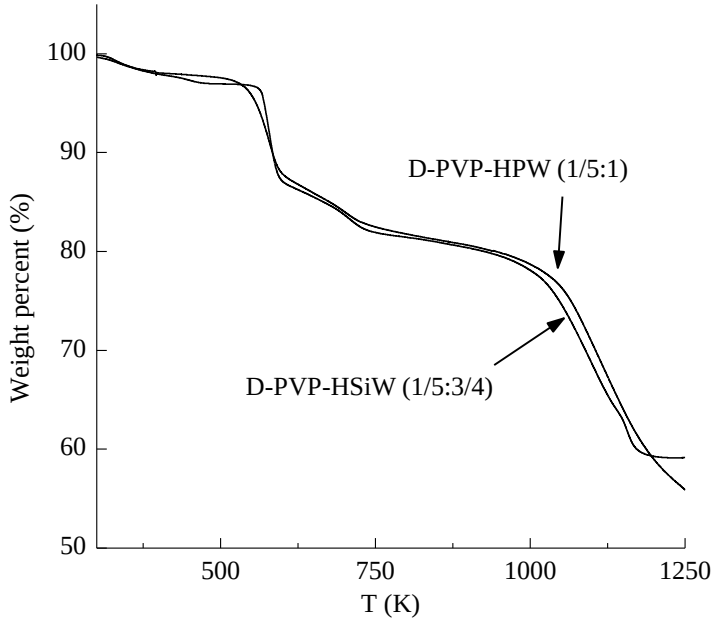

Fig. S9 TG spectra of PVP-HPW (1/5:1) and PVP-HSiW (1/5:3/4)

The thermal stability of the samples was evaluated by a SDT Q600 instrument. The measurement was carried out through temperature ramping rate at 10 K min^{-1} in N_2 flow rate of 10 mL min^{-1}.

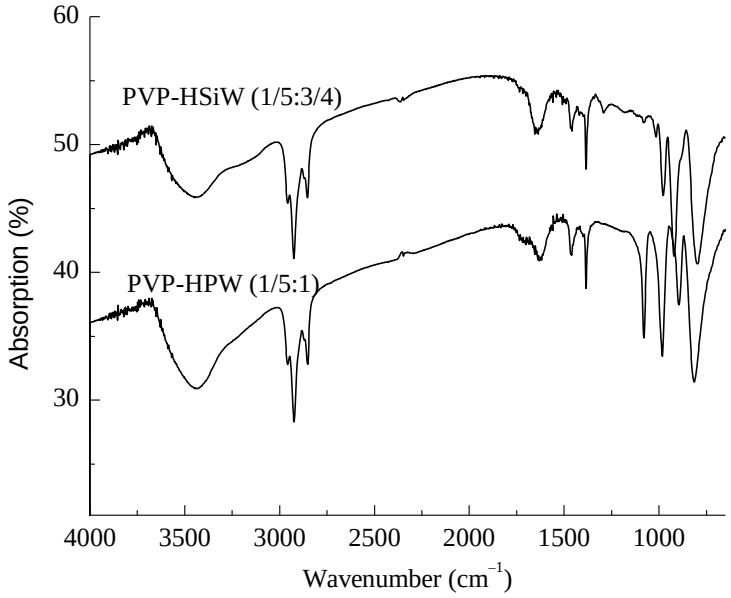

Fig. S10 FTIR spectra of solid residue at the blank experiment.

At the blank experiment without adding substrate, butanol slurry of PVP-HPA was processed at the same reaction condition as that in Table 1. After reaction, the solution was separated from the slurry by centrifugation and the butanol in solution was vapored. The solid residue was collected and measured by FTIR to recognize the molecular composition.

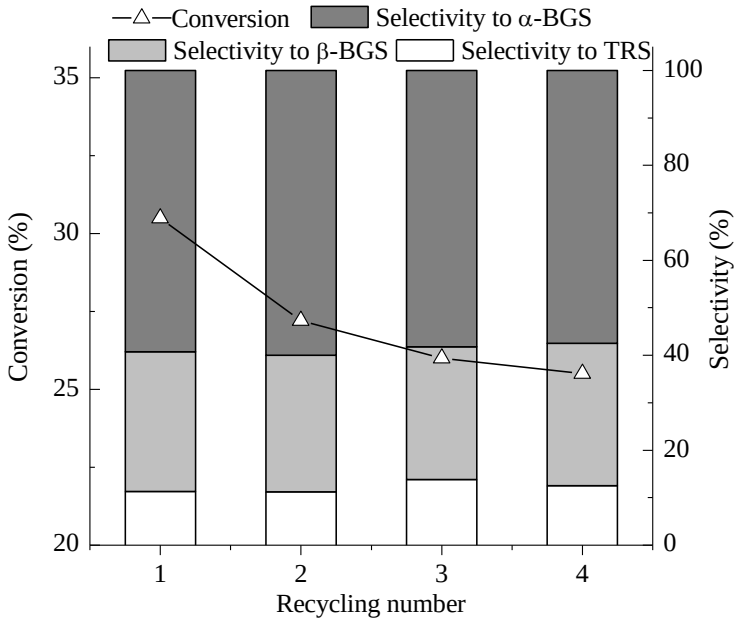

Fig. S11 Testing the recyclability of PVP-HPW (1/5:1) in catalyzing butanolysis of cellobiose at low conversion. The reaction time is only 1 h and the other condition is the same to that in Table 1.

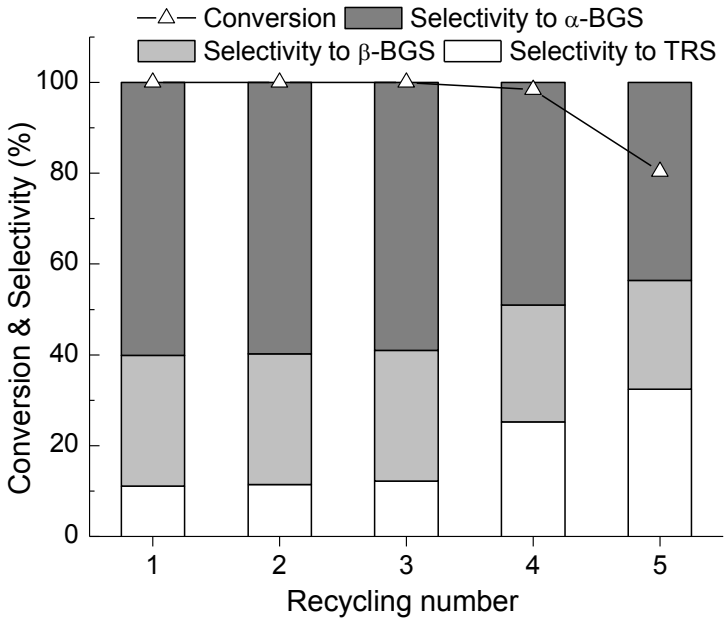

Fig. S12 The recycling performance of PVP-HPW (1/5:1) in catalyzing butanolysis of cellobiose with deliberately adding water. Reaction condition is the same as that in Table 1 except for addition of 200 μL H_2O before each cycle.

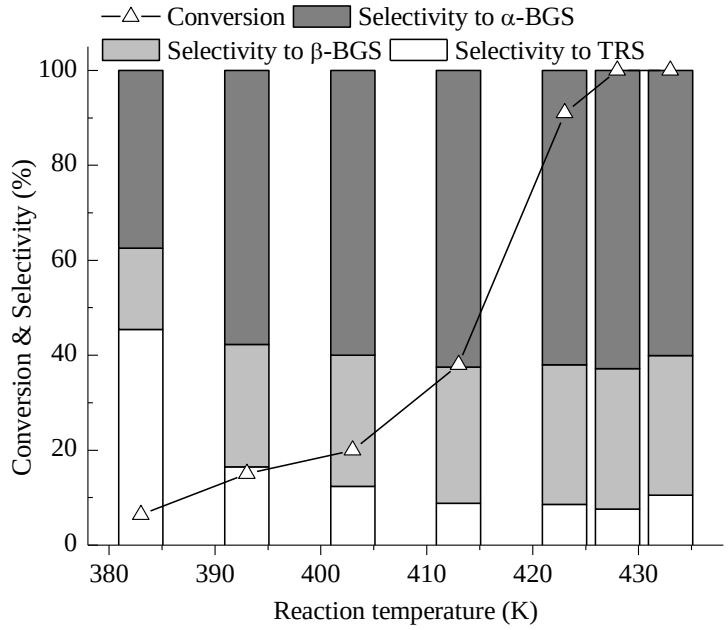

Fig. S13 The catalyzing performance of PVP-HPW (1/5:1) in butanolysis of cellobiose at the different reaction temperature. The reaction condition is the same to that in the Table 1 except for the changing reaction temperature.