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Selective hydrogenolysis of agricultural straw-based cellulose to propylene glycol and acetol over acidic WO_x/ZrO_2

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Characterization

X-ray diffraction (XRD) patterns were tested by Rigaku Ultima IV X-ray diffractometer equipped with Cu Kα radiation operating at 35 kV and 25 mA (λ = 1.5405 Å) scanning from 5° to 90° at a speed of 30° min^{-1}.

The temperature-programmed reduction (H_2-TPR) analysis of WO_3/ZrO_2 catalysts were performed by Micromeritics tp5080 apparatus using a 5%H_2/He mixture (flowing rate: 30 mL·min^{-1}) and a heating rate of 10 K·min^{-1} with a thermal conductor detector (TCD).

Nitrogen sorption isotherms were collected on a BELSORP-MAX instrument, and reduced samples were kept on 77 K after degassing for 10 h under vacuum at 573 K. The special surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Surface density (SD, W/nm^2)=Concentration of W ($g_W/g_{Cat.}$)×Avagodro number (1/(mol W))/BET area (m^2/g Cat.)×Atomic weight of W (g_W/mol_W)×10^{18} (nm^2/m^2)

The transmission electron microscopy (TEM) was measured on the FEI Tecnai G2 F30 microscope (operating at 300 kV).

X-ray photoelectron spectroscopy (XPS) were tested by a Thermo Scientific K-Alpha spectrometer equipped with Al Kα (hν = 1486.6 eV) radiation.

In CO_2/NH_3-TPD measurement, the samples were purged under He flow for 60 min at 723 K. The sample was cooled down to 393 K to be ready for adsorption. After adsorption saturation with purging CO_2/NH_3, the samples were heated from 393 K to 1073 K in He flow at a temperature rate of 10 K/min, and the desorbed NH_3 was monitored by a TCD detector.

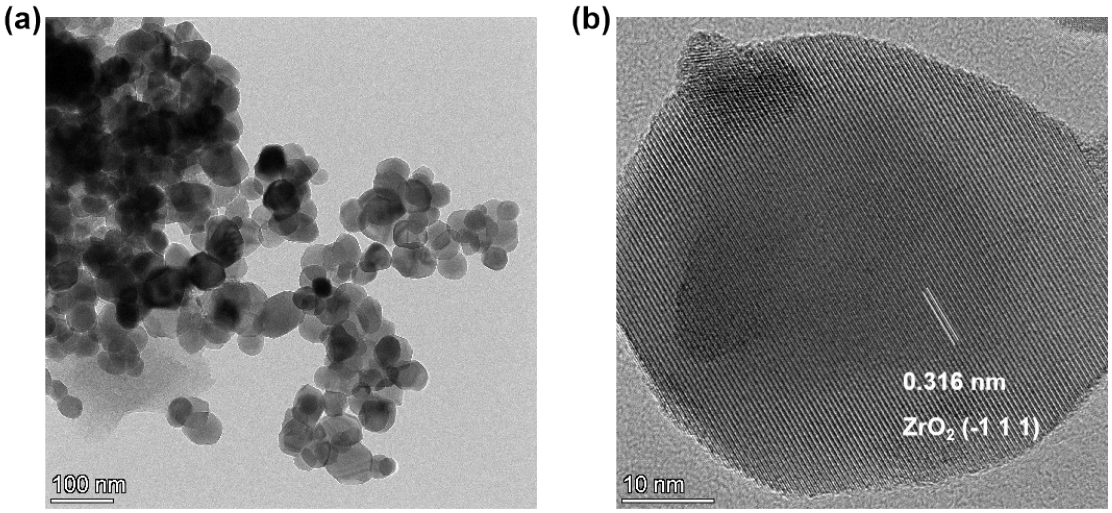

Figure S1. TEM image of WO_x/ZrO_2(600).

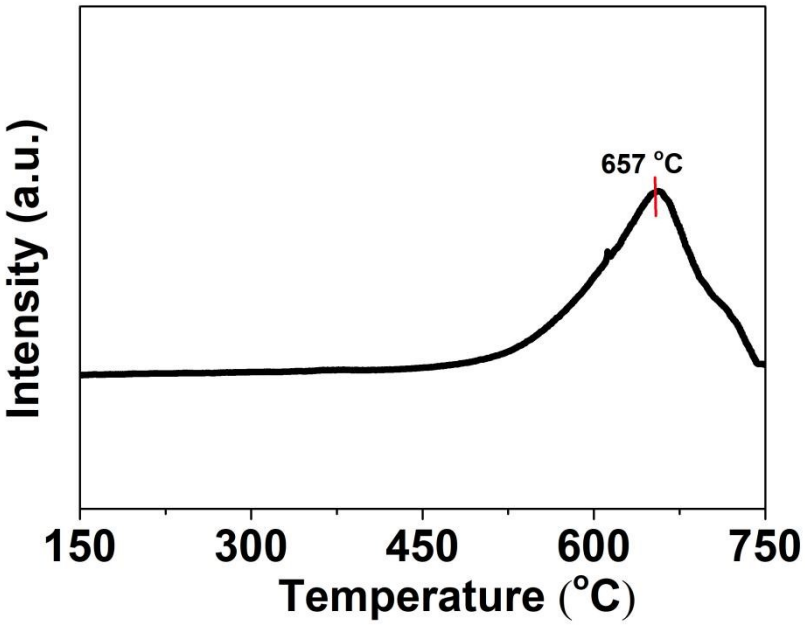

Figure S2. H_2-TPR profile of the WO_3/ZrO_2 sample.

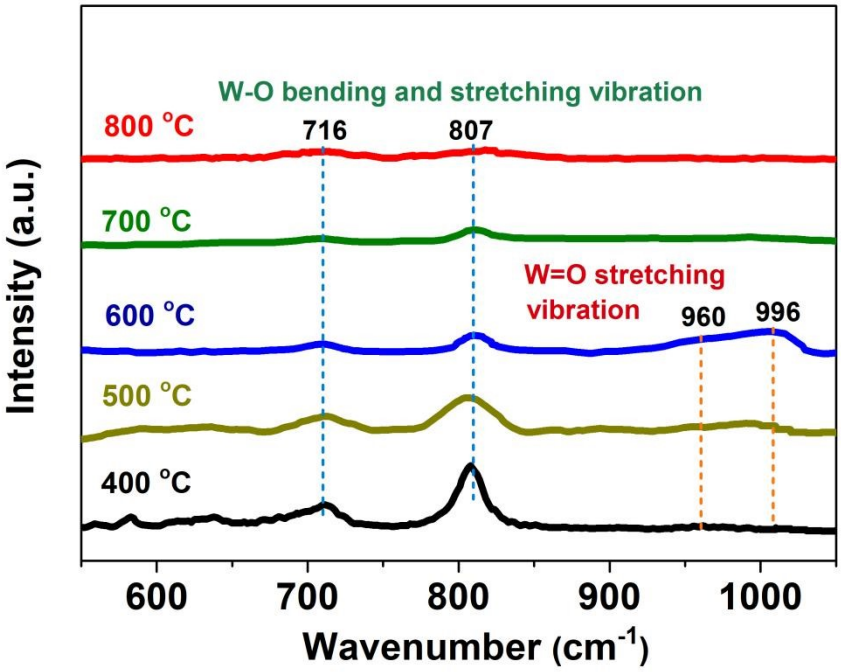

Figure S3. Raman spectra of different WO_x/ZrO_2(T) catalysts.

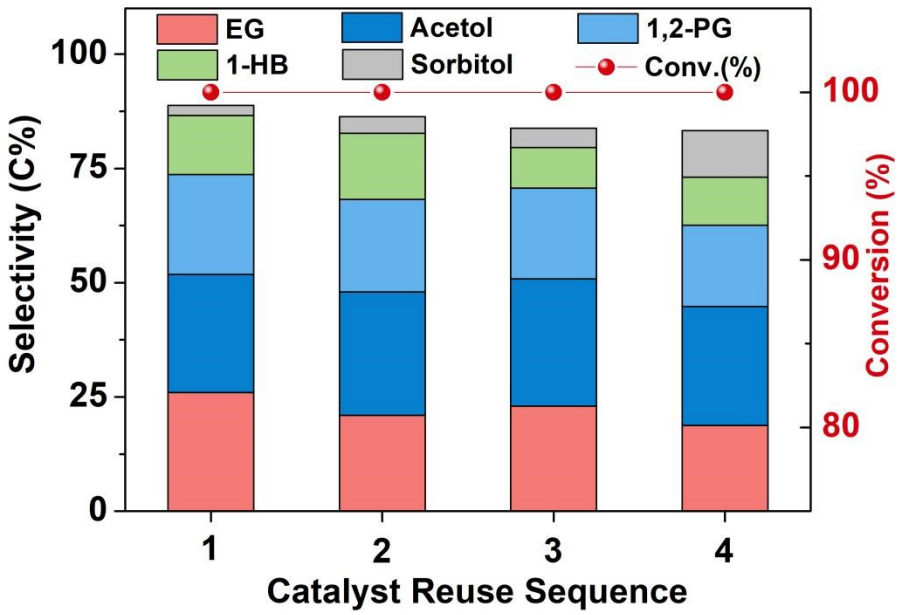

Figure S4. Recycling results of the $WO_x/ZrO_2(600)$ catalyst for cellulose hydrogenolysis. Reaction conditions: cellulose, 1.0 g; 20%$WO_x/ZrO_2(600)$, 0.2 g; 1%Ru/AC catalyst, 0.2 g; H_2O, 100 mL; H_2, 4 MPa; 800 rpm; 240 ^oC; 2 h.

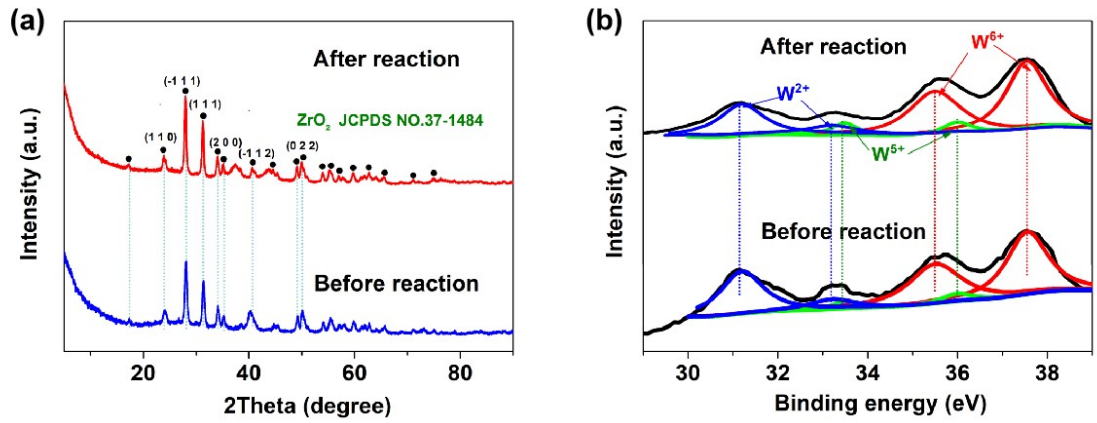

Figure S5. (a) xrd (b) xps spectra of WO_x/ZrO_2(600) catalyst before and after reaction.

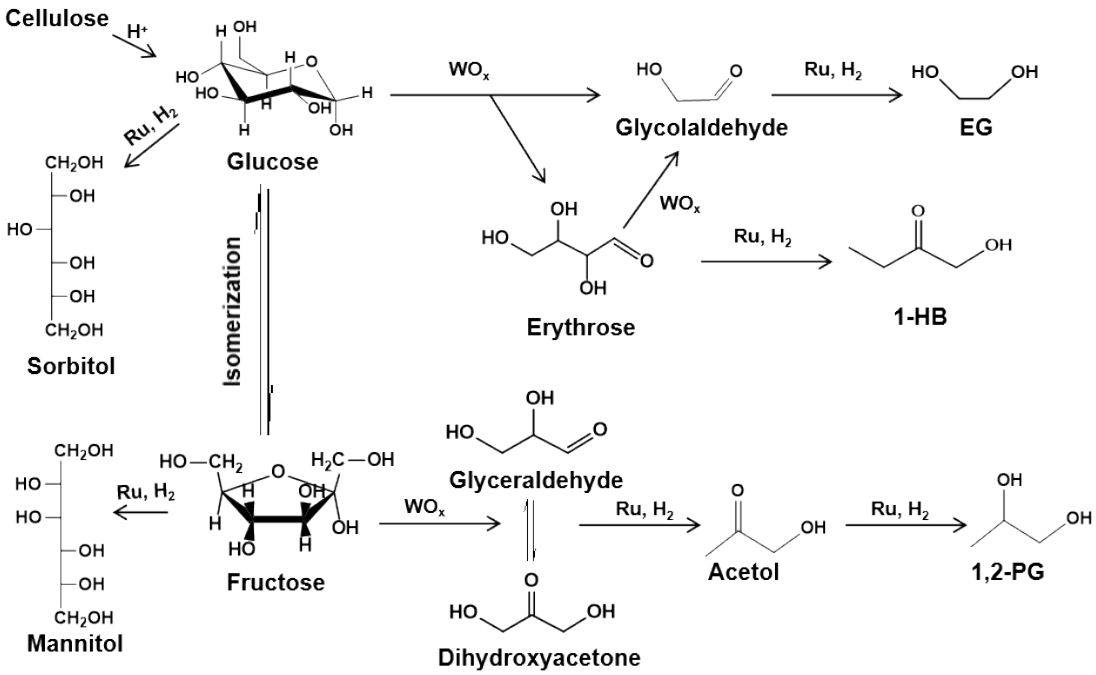

Figure S6. The mechanism of cellulose hydrogenolysis to acetol and 1,2-PG.

Table S1. The evaluation of different catalysts for the retro-aldol condensation of cellulose.

Catalyst	Conv. (C %)	Selectivity (C %)						Carbon balance (%)
		EG	Acetol	1,2-PG	1-HB	Sorbitol	Other	
WO_x/ZrO_2(400)+ Ru/AC	97.1	47.4	7.5	7.7	4.1	12.8	8.2	85.7
WO_x/ZrO_2(500)+ Ru/AC	98.5	45.1	10.1	14.2	8.5	5.6	2.2	85.7
WO_x/ZrO_2(600)+ Ru/AC	100.0	26.0	25.8	21.9	12.9	2.2	6.2	89.9
WO_x/ZrO_2(700)+ Ru/AC	100.0	48.8	8.0	12.8	6.5	3.2	2.0	82.3
WO_x/ZrO_2(800)+ Ru/AC	100.0	58.7	3.0	15.1	1.2	2.3	0.8	82.1

Reaction conditions: cellulose, 1.0 g; 30%WO_x/ZrO_2(T), 0.2 g; 1%Ru/AC catalyst, 0.2 g; H_2O, 100 mL; H_2, 4 MPa; 800 rpm; 240 ^oC; 2 h.

Table S2. The evaluation of different catalysts for the retro-aldol condensation of cellulose.

Catalyst	Conv. (C %)	Selectivity (C %)						Carbon balance (%)
		EG	Acetol	1,2-PG	1-HB	Sorbitol	Others	
WO_x/ZrO_2(600)	88.1	1.2	0	2.1	0	9.1	8.3	20.7
WO_x/ZrO_2(600) + 0.5%Ru/AC	99.0	16.5	19.3	8.2	4.9	3.5	8.1	60.5
WO_x/ZrO_2(600) + 1.0%Ru/AC	100.0	26.0	25.8	21.9	12.9	2.2	6.2	89.9
WO_x/ZrO_2(600) + 1.5%Ru/AC	100.0	19.3	13.4	16.7	9.3	4.1	10.3	73.1
1%Ru/AC	55.2	15.2	0.1	4.3	0.5	28.3	2.2	50.6

Reaction conditions: cellulose, 1.0 g; 30%WO_x/ZrO_2(600), 0.2 g; 1%Ru/AC catalyst, 0.2 g; H_2O, 100 mL; H_2, 4 MPa; 800 rpm; 240 ^oC; 2 h.

Table S3. ICP analysis of metal content of 30%WO_x/ZrO_2(600) + 1%Ru/AC catalyst before and after reaction.

Catalyst	Ru loading (wt %)	W loading (wt %)
Fresh	1.0	30.3
After 4 runs	1.0	26.9

Reaction conditions: cellulose, 1.0 g; 30%WO_x/ZrO_2(600), 0.2 g; 1%Ru/AC catalyst, 0.2 g; H_2O, 100 mL; H_2, 4 MPa; 800 rpm; 240 ^oC; 2 h.

Table S4. Catalytic conversion of glucose catalyzed by WO_x/ZrO_2(T) catalysts.

Catalyst	Conv. (C %)	Selectivity (C %)	
		Fructose	Others
WO_x/ZrO_2(400)+Ru/AC	24.3	66.1	9.9
WO_x/ZrO_2(500)+Ru/AC	24.7	64.5	10.9
WO_x/ZrO_2(600)+Ru/AC	26.8	75.5	13.1
WO_x/ZrO_2(700)+Ru/AC	18.1	73.8	6.1
WO_x/ZrO_2(800)+Ru/AC	14.6	55.9	11.8

Reaction conditions: 1 g glucose, 0.2 g catalyst, 50 ML DI-water, 120 ^oC, 2 h.