Electronic Supplementary Information

Direct conversion of cellulose into ethanol catalysed by a combination of tungstic acid and zirconia-supported Pt nanoparticles

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Experimental details

Materials and catalyst preparation

Tungstic acid and metal oxides including ZrO_2, SiO_2, Al_2O_3, TiO_2 and MgO with purities >99% were purchased from Sinopharam Chemical Reagent Co. Ltd or Alfa Aesar. Organic compounds such as cellulose, cellobiose, starch, glucose, fructose, glycerol, glycoaldehyde, glyceraldehyde, 1,2-propandiol, ethylene glycol and ethanol were purchased from Alfa Aesar.

Catalysts were prepared by an impregnation method. In a typical procedure for the preparation of Pt/ZrO_2, ZrO_2 was added into an aqueous solution of H_2PtCl_6, followed by stirring for 4 h. After water was removed by evaporation at 353 K under stirring, the sample was further dried at 353 K for 12 h to obtain the precursor. Then, the Pt/ZrO_2 catalyst was obtained by calcining the precursor in air at 623 K for 2 h, followed by reduction in H_2 at the same temperature for 2 h. The same procedure was applied to the preparation of Pt nanoparticles loaded on other supports and different metal catalysts loaded on ZrO_2. For comparison, the Pt/ZrO_2-c was obtained by calcining the precursor in air at 623 K for 2 h and the Pt/ZrO_2-r catalyst was obtained by reducing the Pt/ZrO_2-c catalyst in H_2 at 723 K. Pt/ZrO_2-b catalyst was prepared by a solution-reduction method, which includes the reduction of H_2PtCl_6 using $NaBH_4$ as a reducing agent at room temperature and a subsequent adsorption of the formed Pt nanoparticles onto ZrO_2.

Catalyst characterization

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out with an Agilent ICP-MS 4500 instrument to measure the actual loading amount of Pt in each catalyst. Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of suspensions were applied on a copper grid coated with carbon. The mean size of Pt nanoparticles were estimated by counting about 200 particles from the TEM images. Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'Pert Pro Super X-ray diffractometer equipped with X'Celerator detection system. The Cu K_α radiation (40 kV and 30 mA) was used as the X-ray source. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K_α radiation (1846.6 eV) as the X-ray source. The diffuse reflectance Fourier-transform infrared (FT-IR) spectroscopy was measured on a Nicolet 6700 spectrometer. For CO-adsorbed FT-IR study, the catalyst was loaded into the IR cell and calcined at 473 K for 1 h in N_2 flow. After cooling to 303 K in N_2, a spectrum was collected as the background. Subsequently, CO was introduced into the cell and the adsorption of CO was conducted at 303 K for 30 min, and then a spectrum was recorded after fluxing the cell with N_2 flow. The spectrum of CO adsorbed on the surface of catalysts was obtained by subtracting these spectra.

Catalytic reaction

Catalytic conversions of cellulose, carbohydrates and some related compounds were performed in a Parr4848 autoclave reactor. As an example for the conversion of cellulose, the catalyst and the powdery cellulose were added to the reactor, which had been pre-charged with deionized H_2O. After purging with H_2 for five times, the reactor was charged with H_2 at a pressure of 4 MPa at room temperature. When the system reached the reaction temperature (typically 523 K), the reaction was initiated by vigorous stirring. After a reaction fixed time (typically, 5 h), the reaction was quickly terminated by cooling the reactor to room temperature in cold water. For the recycling uses of Pt/ZrO_2, the recovered catalyst after removing possible organic residues on its surface was used for the next reaction. Gas products were analysed by two chromatographs, which were equipped with two thermal conductivity detectors (TCDs) and a flame ionization detector (FID). A Porapak Q column was used for the separation of CO, CH_4, CO_2 and C_2H_4. A Rt-Q-Bond column in connection with the FID was used to separate and analyze CH_4, C_2H_6, C_3H_8 and C_4H_{10}. Liquid products were quantified using a high-performance liquid chromatograph (HPLC, Shimazu LC-20A) equipped with an RI detector and a Shodex SUGARSH-1011 column (8×300 mm) using

a dilute H_2SO_4 aqueous solution as the mobile phase. The conversion was calculated on the basis of the mole difference between the substrate before and after each reaction. The yields of main products, such as ethanol, ethylene glycol, glycerol, 1,2-propandiol and propanol were calculated from the percentage of carbon moles in products divided by the total carbon moles in the substrate. In most cases, the carbon balance was in a range of 80-96%.

Table S1 Conversion of cellulose in aqueous medium in the presence of Pt/ZrO_2 and H_2WO_4 with different amounts.

H_2WO_4 amount (g)	Conv. (%)	Selectivity (%)							Carbon balance
		Sorbitol	EtOH	EG	1,2-PD	PrOH	Glycerol	Others	
0	100	17	2.2	2.0	4.4	0	1.2	73	43
0.01	100	10	19	16	3.0	6.7	3.6	41	89
0.03	100	3.2	25	23	2.4	7.5	4.2	34	92
0.05	100	0	32	24	3.2	5.6	3.0	32	94
0.1	100	0	33	24	3.5	7.8	3.3	28	96

Reaction conditions: cellulose, 0.20 g; Pt/ZrO_2 (Pt loading, 2.0 wt%), 0.10 g; H_2O, 20 ml; $P(H_2)$, 4 MPa; temperature, 523 K; time, 5 h. EtOH, EG, 1,2-PD and PrOH denote ethanol, ethylene glycol, 1,2-propandiol and propanol, respectively. Others include methanol, C_1-C_4 alkanes and unknown products.

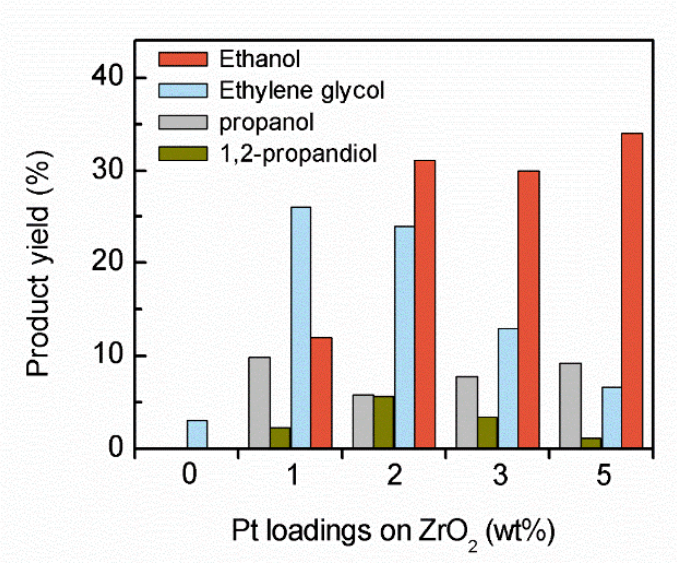

Fig. S1 Effect of Pt loading amount on catalytic behaviour of Pt/ZrO_2 in combination with H_2WO_4 for conversion of cellulose. Reaction conditions: cellulose, 0.20 g; Pt/ZrO_2 (Pt loading, 0-5.0 wt%), 0.10 g; H_2WO_4, 0.050 g; H_2O, 20 ml; $P(H_2)$, 4 MPa; temperature, 523 K; time, 5 h.

Table S2 Catalytic performances of ZrO_2-supported different metals in combination with H_2WO_4 for conversion of cellulose.

Catalyst	Product yield (%)					
	EtOH	EG	1,2-PD	PrOH	Glycerol	Others
Ru/ZrO_2	11	45	7.5	3.3	2.2	31
Pd/ZrO_2	12	20	13	2.4	7.5	45
Rh/ZrO_2	14	14	18	5.6	8.6	39
Ir/ZrO_2	14	7.7	12	5.1	14	47

Reaction conditions: cellulose, 0.20 g; metal/ZrO_2 (metal loading, 2.0 wt%), 0.10 g; H_2O, 20 ml; $P(H_2)$, 4 MPa; temperature, 523 K; time, 5 h. EtOH, EG, 1,2-PD and PrOH denote ethanol, ethylene glycol, 1,2-propandiol and propanol, respectively. Others include methanol, C_1-C_4 alkanes and unknown products.

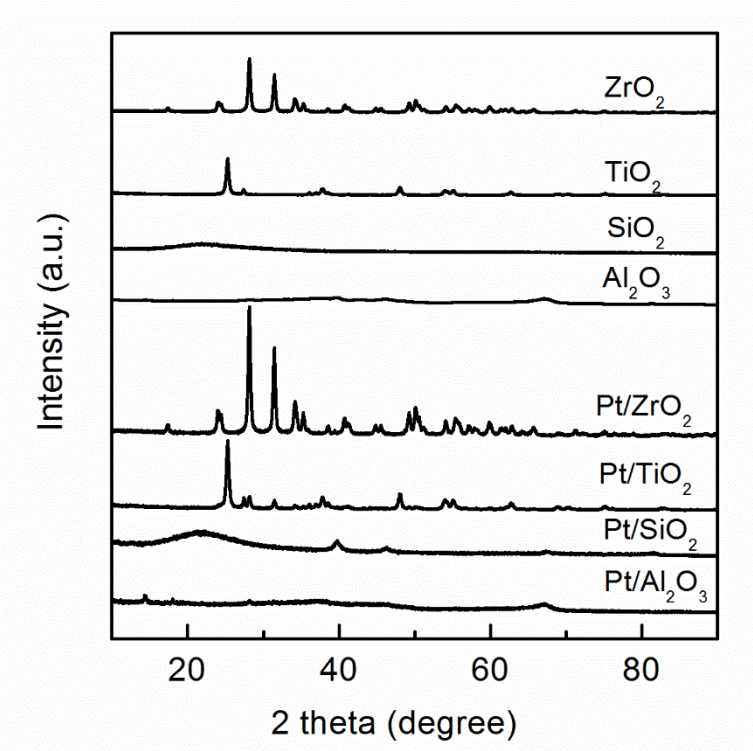

Fig. S2 XRD patterns of different metal oxides and metal oxide-supported Pt catalysts.

Table S3 Some physical properties for Pt nanoparticles loaded on different metal oxides.

Catalyst	Pt loadings (wt%)[a]	Surface area ($m^2\ g^{-1}$)[b]	Pore volume ($cm^3\ g^{-1}$)[b]
Pt/ZrO_2	2.0	43	0.15
Pt/Al_2O_3	1.9	229	0.21
Pt/SiO_2	1.9	397	0.45
Pt/TiO_2	2.0	51	0.25
Pt/MgO	2.0	26	0.10

[a] Determined by ICP-MS. [b] Obtained by N_2 adsorption measurements.

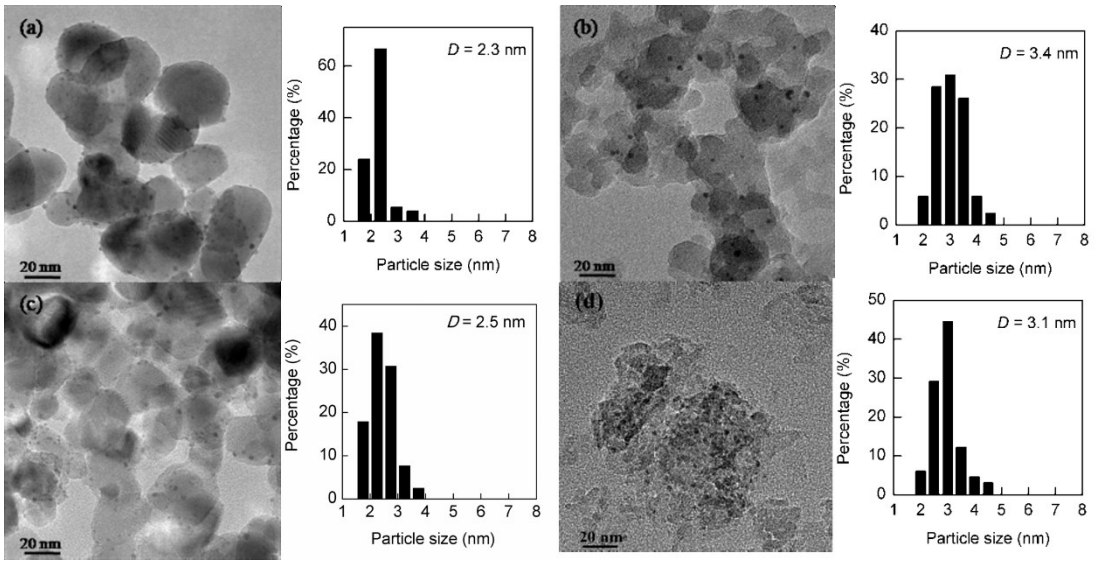

Fig. S3 TEM micrographs and Pt particle size distributions. (a) Pt/ZrO_2. (b) Pt/SiO_2. (c) Pt/TiO_2. (d) Pt/Al_2O_3.

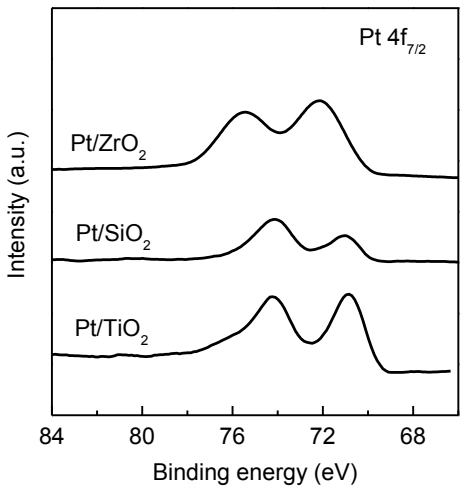

Fig. S4 Pt 4f XPS spectra for Pt/ZrO_2, Pt/SiO_2 and Pt/TiO_2 catalysts.

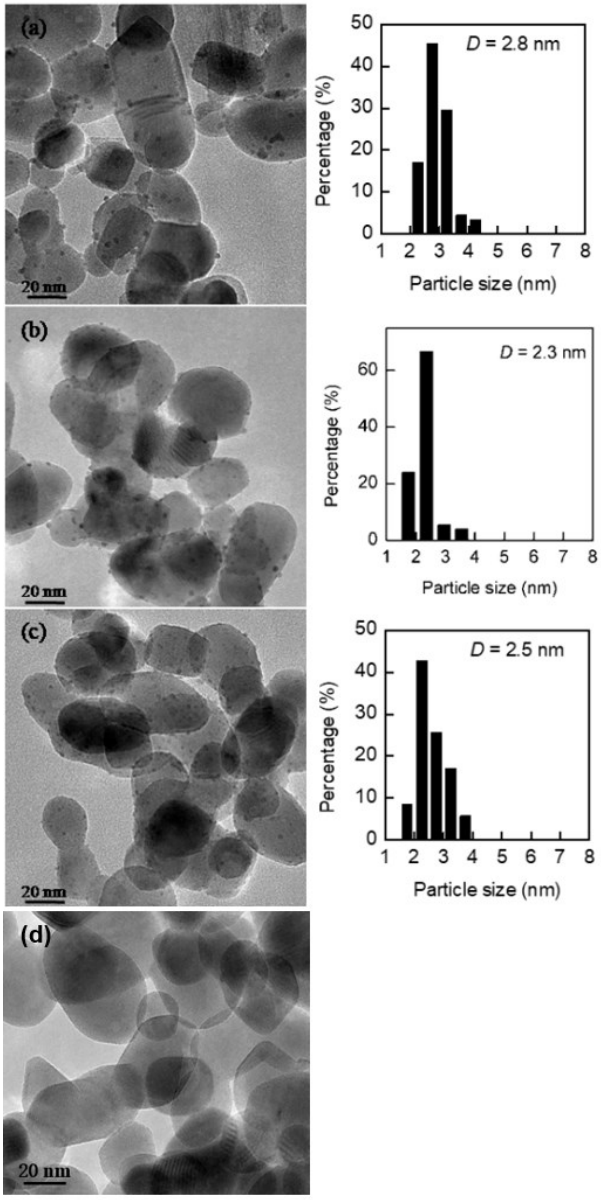

Fig. S5 TEM micrographs and Pt particle size distributions. (a) Pt/ZrO_2-c. (b) Pt/ZrO_2. (c) Pt/ZrO_2-r. (d) ZrO_2.

Table S4 Deconvolution results for Pt 4f XPS spectra.[a]

Catalyst	Percentage of Pt species (%)		
	Pt^0 (71.1 eV)	Pt^{2+} (72.6 eV)	Pt^{4+} (74.9 eV)
Pt/ZrO_2-c	0	70	30
Pt/ZrO_2-c[b]	84	16	0
Pt/ZrO_2	30	70	0
Pt/ZrO_2-r	73	27	0
Pt/ZrO_2-b	94	6	0

[a] Calculated from Pt $4f_{7/2}$ XPS spectra in Figure 2B or Fig. S6. [b] The used catalyst.

Table S5. Gas-phase products observed for the conversion of cellulose over different catalysts.

Catalyst	Yield (%)				Total yield (%)
	methane	ethane	propane	butane	
Pt/ZrO_2-c	0.10	2.4	5.5	13	22
Pt/ZrO_2	0.28	3.1	7.0	16	26
Pt/ZrO_2-r	0.40	6.5	9.8	19	36
Pt/ZrO_2-b	0.64	9.8	10	25	46

Reaction conditions: cellulose, 0.2 g; catalyst (Pt loading, 2.0 wt%), 0.10 g; H_2WO_4, 0.050 g; H_2O, 20 ml; $P(H_2)$, 4 MPa; temperature, 523 K; time, 5 h.

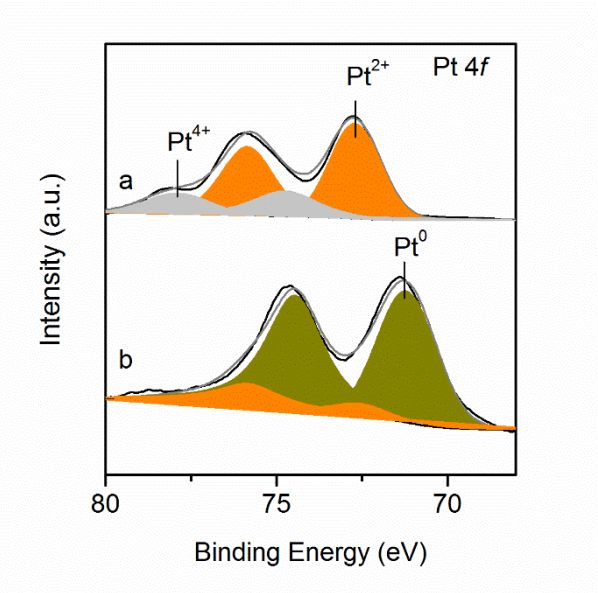

Fig. S6 XPS spectra of Pt 4f for Pt/ZrO_2-c. a fresh. b used.

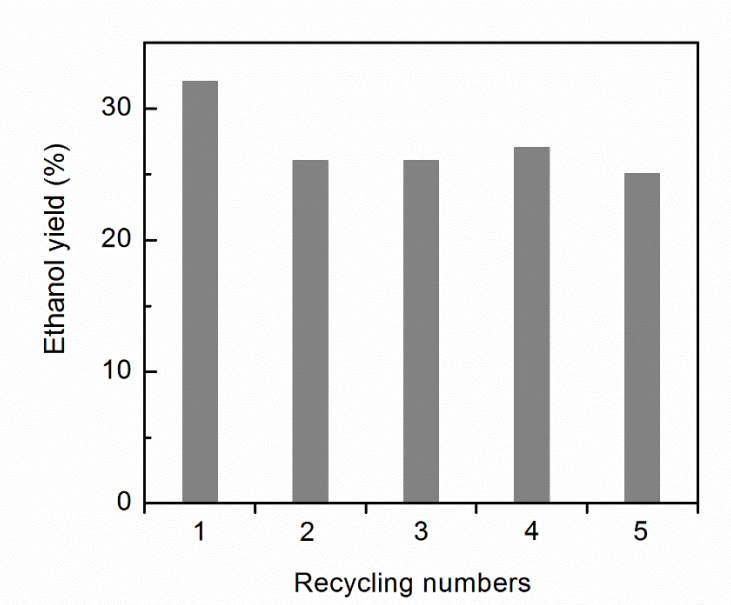

Fig. S7 Recycling uses of Pt/ZrO_2 in combination with H_2WO_4 for conversion of cellulose. Reaction conditions: cellulose, 0.20 g; H_2WO_4, 0.05 g; Pt/ZrO_2 (Pt loading, 2.0 wt%), 0.10 g; $P(H_2)$, 4 MPa; H_2O, 20 mL; temperature, 523 K; time, 5 h.

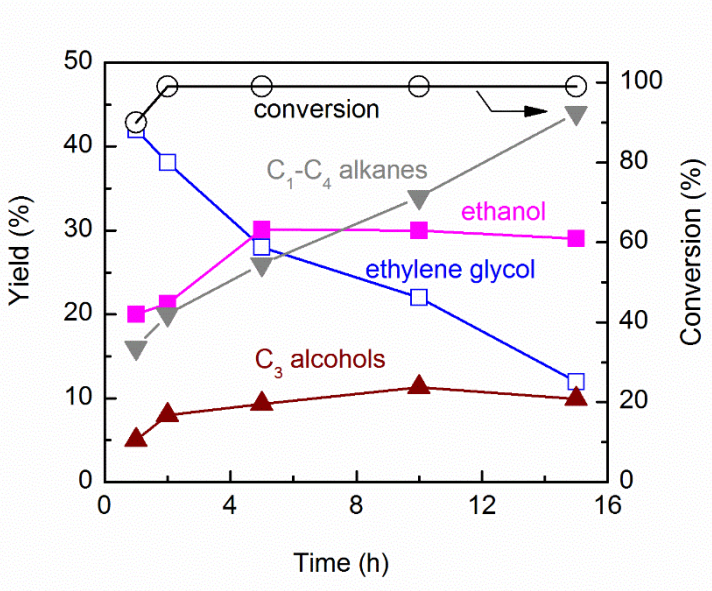

Fig. S8 Time course for the conversion of cellulose catalysed by Pt/ZrO_2 in combination with H_2WO_4. Reaction conditions: cellulose, 0.20 g; H_2WO_4, 0.05 g; Pt/ZrO_2 (Pt loading, 2.0 wt%), 0.10 g; $P(H_2)$, 4 MPa; H_2O, 20 mL; temperature, 523 K.