

Supplementary Information

One-pot chemocatalytic transformation of cellulose to ethanol over

Ru-WO_x/HZSM-5

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Experimental details

1. Reagents

α -Cellulose (particle size = 25 μm), bicyclohexane (AR, >99%), Ruthenium trichloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) (AR, 35.0-42.0%), ammonium metatungstate (AR, >99%) were purchased from Aladdin Chemical Reagent Co., Ltd; high-pure H_2 and high-pure N_2 were purchased from Nanjing Special Gas Factory Co. Ltd. HZSM-5 was purchased from the Catalyst Plant of Nankai University. Bagasse and corn stalk were purchased from Guangxi Guigang Ganhua Inc., China. All these chemicals were used without further purification.

2. Catalysts Preparation

A series of Ru- WO_x /HZSM-5 catalysts with different amounts of Ru loading and Ru/W mass ratios were prepared by co-impregnation method. The catalysts were labeled as (x)Ru-(y) WO_x /HZSM-5 (x, y refer the mass percentage of Ru and W, respectively). A typical catalyst preparing procedure was as follows: 1.2 g of HZSM-5 was added into 100 g of deionized water in a 250 mL round-bottom flask and stirred at 60 $^\circ\text{C}$. A certain amount of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and a pre-calculated amount of ammonium metatungstate were well dissolved in deionized water (5 g) and then dropwise added into the above catalyst/water mixture under magnetic stirring. The mixture was stirred vigorously for 24 h. After that, water is removed by rotary evaporator. Subsequently, the solid was transferred into an oven and dried at 105 $^\circ\text{C}$ for 12 h. After drying, the samples were reduced in H_2 atmosphere at 600 $^\circ\text{C}$ for 2 h with a heating rate of 1 $^\circ\text{C min}^{-1}$ before reaction. The Ru and W content was measured by ICP-AAS of PerkinElmer Corporation AA800.

3. Catalyst characterization

The temperature-programmed reduction (H_2 -TPR) was carried out in a home-built reactor system coupled to a gas chromatograph. Before TPR tests, the samples were pretreated in Ar flow at 200 $^\circ\text{C}$ for 1 h. The TPR was carried out in a 5% H_2 /Ar mixture gas flow from 40 $^\circ\text{C}$ to 800 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C/min}$. The liquid nitrogen/ethanol cooling bath was used to remove the moisture from the effluent stream

before the stream entered a thermal conductivity detector (TCD).

The temperature-programmed desorption was carried out in a home-built reactor system coupled to a gas chromatograph. All the gas flow was set to 40 mLmin⁻¹. Temperature-programmed desorption of ammonia (NH₃-TPD) was employed to determine the total acidity of the catalysts. Prior to absorption of ammonia, 100 mg of catalyst sample was heated at 500 °C for 1 h under Ar flow and then cooled to 80 °C followed by saturating with pure NH₃ for 1 h. After flushing with Ar for 1h, the NH₃-TPD was performed from 80 °C to 800 °C with a heating rate of 10 °C min⁻¹. The desorbed ammonia was monitored by an on-line gas chromatograph equipped with a thermal conductivity detector (TCD).

The transmission electron microscopy (TEM) image and fast Fourier transform (FFT) diffraction of the HRTEM image were taken with a JEOL n JEM 2011F apparatus operating at 200 kV voltages. Before being transferred into the TEM chamber, the samples dispersed with ethanol for 30 min were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator.

The powder X-ray diffraction (XRD) patterns of the catalysts were measured by an X'pert (PANalytical) diffractometer, using CuK α radiation at 40 kV and 40 mA, 2 θ ranges were 10°-70°.

The X-ray photoelectron spectroscopy (XPS) spectra was obtained with an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific, USA) at room temperature under a vacuum of 10⁻⁸-10⁻⁹ Torr using monochromated Al K α radiation (1486.92 eV). The binding energies (BE) were calibrated to carbon with a C 1s band at 284.6 eV.

The chemical composition of catalysts was analyzed by an Optima 7300 DV ICP-AAS. ICP-AAS was performed on a PerkinElmer Corporation Analyst 800 instrument. The catalyst sample handling process is as follows: 10 mg of catalyst was added into a 10 mL round-bottom flask with 4 mL of aqua regia and stirred at 80 °C for 24 h until metal is completely dissolved. Then the mixture was diluted to 25 mL in a volumetric flask for characterization

3. Catalyst Catalyst Test

All catalytic reactions for the hydrogenation of cellulose to ethanol were performed in a 25 mL Parr reactor purchased from Anhui Kemi Machinery Technology Co., Ltd. In a typical experiment, 100 mg of cellulose, 120 mg of the reduced catalyst and solvent (10 mL of water) were added into the reactor. After purged for 4 times, H₂ was filled to corresponding pressure at ambient temperature. The reaction temperature and the reaction time were kept at certain values with magnetic stirring. After the reaction, the reactor was cooled to room temperature, and the products were washed with methanol. Finally, the collected sample solution was identified by a gas chromatograph-mass spectrometer combination (GC-MS, Agilent 5975C) and quantified by a gas chromatograph (Kexiao 1690) with HP-INNOWAX capillary column (30 m*0.250 mm*0.25 μm). The GC detecting conditions were as follows: nitrogen as carrier gas; injection port temperature: 280 °C; detector (FID) temperature: 280 °C; column temperature: 40 °C, heating up to 250 °C with a heating rate of 10 °C/min. Bicyclohexane was used as internal standard to quantify the products. In this paper, the experiments were repeated for three times and the data were the average value with experimental error less than 3%.

The conversion and yield were calculated as follows.

$$\text{Yield (\%)} = \frac{\text{mass of carbon transferred from cellulose to the target product}}{\text{mass of carbon in cellulose put into the reactor}} \times 100\%$$

$$\text{Conv. (\%)} = \left(1 - \frac{\text{mass of carbon in cellulose after reaction}}{\text{mass of carbon in cellulose put in the reactor}} \right) \times 100\%$$

4. Results and Discussion

Table S1 Physico-chemical properties of the catalysts.

| Catalyst | BET surface area (m ² g ⁻¹) | Pore volume (cm ³ g ⁻¹) |
|---------------------------------|--|--|
| HZSM-5 | 262.4990 | 0.0924 |
| 5%Ru/HZSM-5 | 231.5561 | 0.0897 |
| 25% WO _x /HZSM-5 | 188.5120 | 0.0904 |
| 1%Ru-25%WO _x /HZSM-5 | 193.7082 | 0.0701 |
| 3%Ru-25%WO _x /HZSM-5 | 226.8699 | 0.0801 |
| 5%Ru-25%WO _x /HZSM-5 | 240.0207 | 0.0915 |
| 5%Ru-15%WO _x /HZSM-5 | 224.6989 | 0.0786 |
| 5%Ru-35%WO _x /HZSM-5 | 193.3502 | 0.0778 |

Table S2. ICP analysis of Ru and W species in 5Ru-25WO_x/HZSM-5 catalyst after reaction.

| Runs | Ru percentage in 5%Ru- 25%WO _x /HZSM-5 (wt%) | W percentage in 5%Ru- 25%WO _x /HZSM-5 (wt%) | Ru Leaching (wt%) | W Leaching (wt%) |
|---------------------|--|---|----------------------|---------------------|
| Fresh | 4.42 | 24.83 | --- | --- |
| 1 st run | 4.39 | 24.56 | 0.03 | 0.27 |
| 2 nd run | 4.33 | 21.67 | 0.09 | 3.16 |
| 3 rd run | 4.32 | 21.24 | 0.10 | 3.59 |
| 4 th run | 4.24 | 20.77 | 0.18 | 4.06 |

Table S3. Relative acid amount of various Ru-WO_x/HZSM-5 samples based on NH₃-TPD.

| Entry | Sample | Relative Acid amount ^a |
|-------|-------------------------------|-----------------------------------|
| 1 | HZSM-5 | 2969 |
| 2 | 25WO _x /HZSM-5 | 2996 |
| 3 | 1Ru-25WO _x /HZSM-5 | 2314 |
| 4 | 3Ru-25WO _x /HZSM-5 | 2305 |
| 5 | 5Ru-25WO _x /HZSM-5 | 2298 |
| 6 | 5Ru-15WO _x /HZSM-5 | 2259 |
| 7 | 5Ru-35WO _x /HZSM-5 | 2280 |

a. The relative acid amount is calculated by integrating the NH₃-TPD curves in Figure S2 using data before 500 °C.

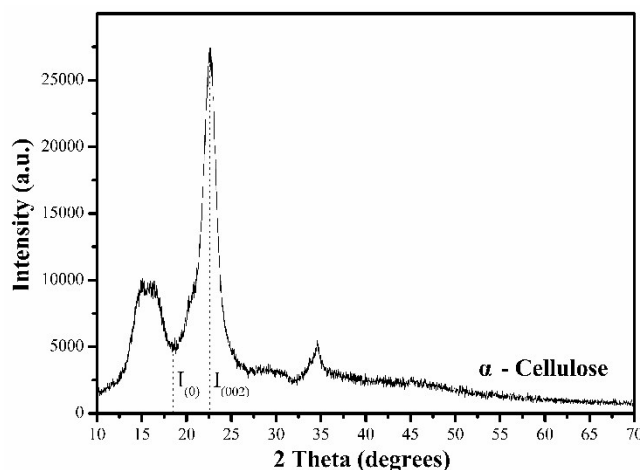


Figure S1. The crystallinity of cellulose.

The crystallinity is calculated by Segal method as shown in Figure S1. The maximal value at about 22.8 degree is measured as $I(002)$, while the minimal value at about 18.8 degree is measured as $I(0)$. The crystallinity equals to $1 - I(0)/I(002)$. The crystallinity of cellulose in our experiment is 83.9%.

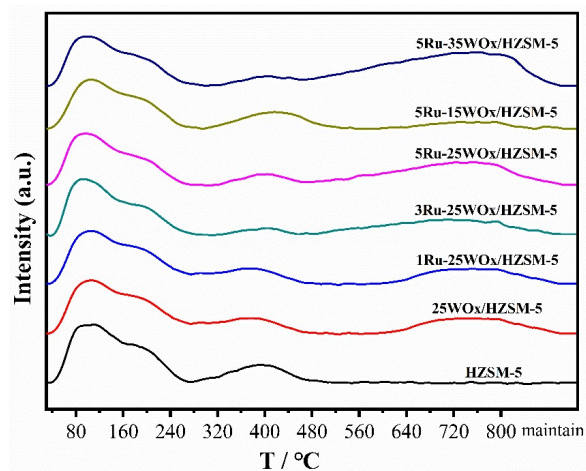


Figure S2. NH_3 -TPD profiles of Ru- WO_x /HZSM-5 samples.

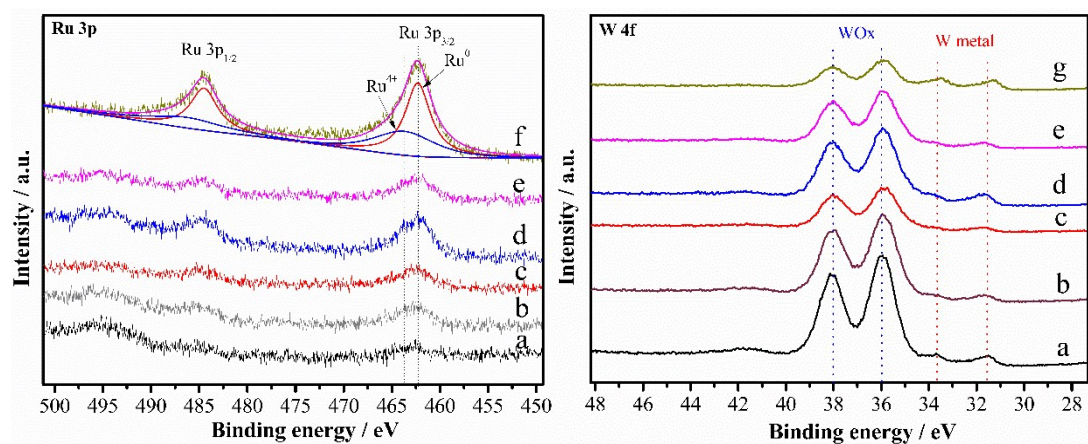


Figure S3. XPS spectra of Ru 3p and W 4f in (a) 1Ru-25WO_x/HZSM-5, (b) 3Ru-25WO_x/HZSM-5, (c) 5Ru-25WO_x/HZSM-5, (d) 5Ru-15WO_x/HZSM-5, (e) 5Ru-35WO_x/HZSM-5, (f) 5Ru/HZSM-5 and (g) 25WO_x/HZSM-5.

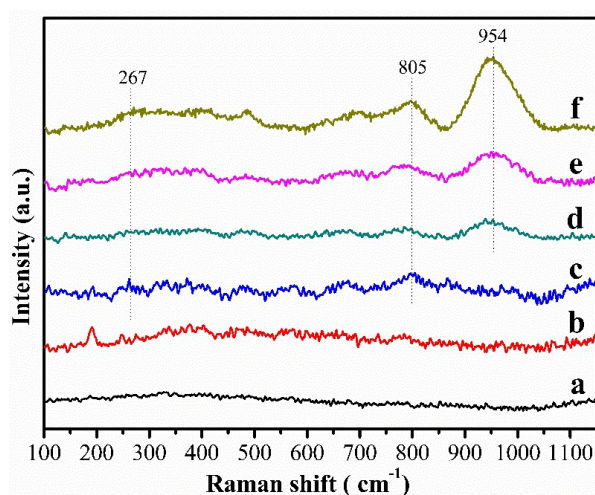


Figure S4. Raman spectra of reduced catalysts: (a) HZSM-5, (b) 5Ru/HZSM-5, (c) 25WO_x/HZSM-5, (d) 5Ru-15WO_x/HZSM-5, (e) 5Ru-25WO_x/HZSM-5, and (f) 5Ru-35WO_x/HZSM-5.

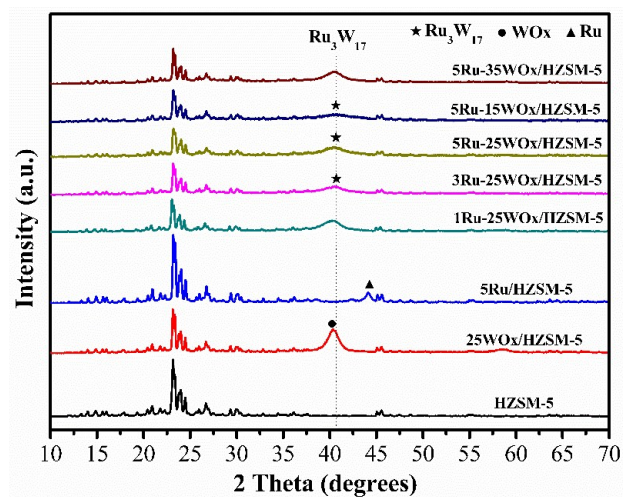


Figure S5. XRD patterns of the as-reduced Ru-WO_x/HZSM-5 catalysts.

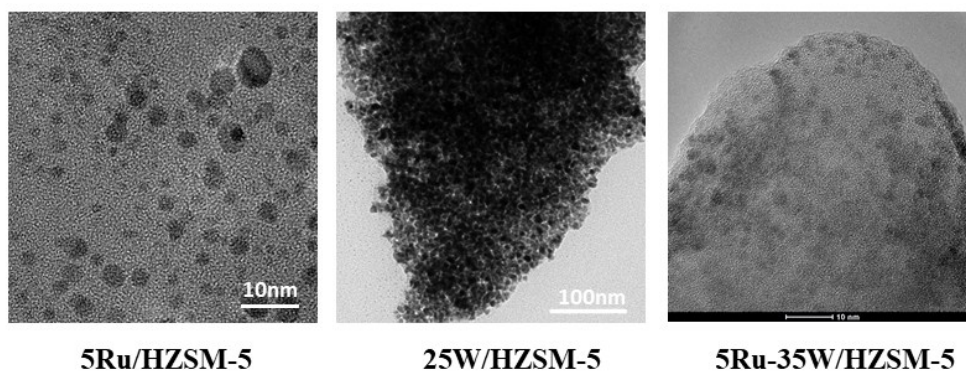


Figure S6. TEM images of 5Ru/HZSM-5, 25WO_x/HZSM-5 and 5Ru-35WO_x/HZSM-5 catalysts.

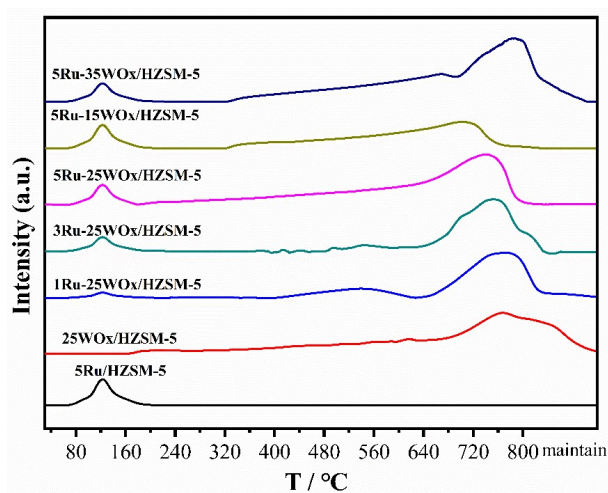


Figure S7. H₂-TPR profiles of Ru-WO_x/HZSM-5 samples.

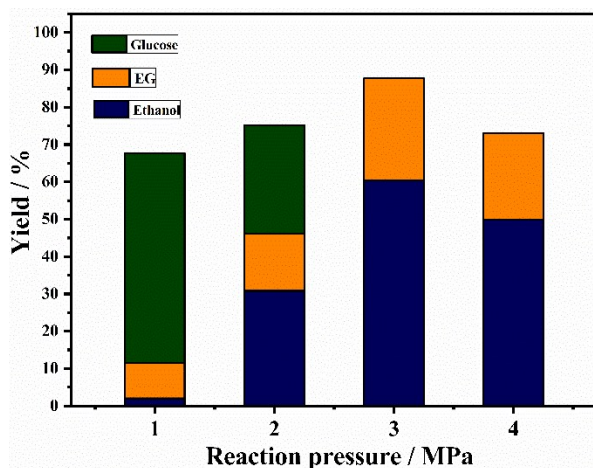


Figure S8. Effect of reaction hydrogen pressure. 100 mg of catalyst, 100 mg of cellulose, 10 mL of water as solvent, 235 °C, 10 h, and 800 rpm. EG: ethylene glycol. Others include some unidentified products and humins.

Recycling experiments over Ru-WO_x/HZSM-5 catalyst.

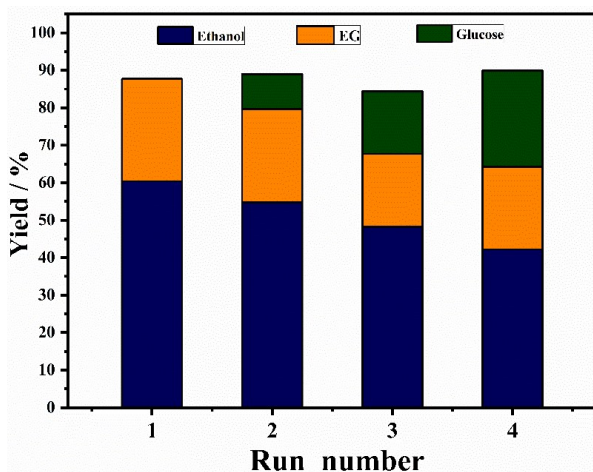


Figure S9. The recycling experiments for the catalytic conversion of cellulose to ethanol over 5Ru-25WO_x/HZSM-5 catalyst. Reaction conditions: 100 mg of catalyst, 100 mg of cellulose, 10 mL of water as solvent, 235 °C, 3 MPa H₂, 10 h, and 800 rpm.

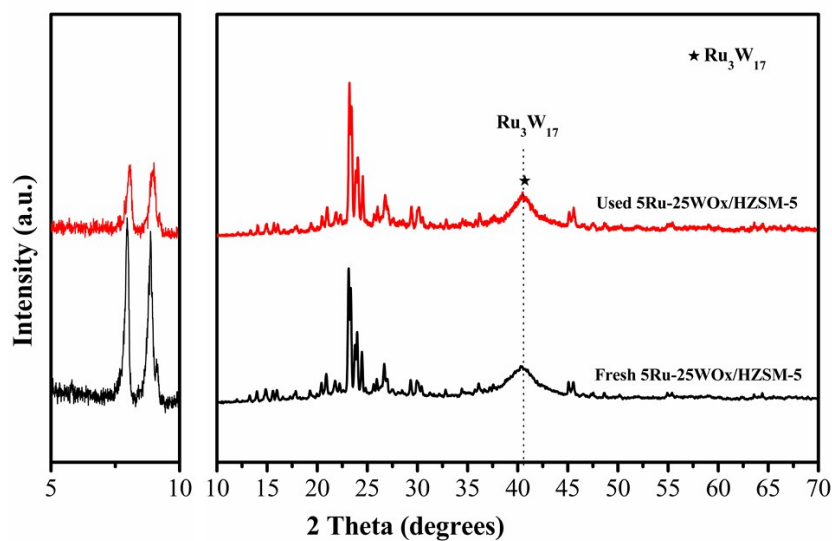


Figure S10. The XRD patterns for both fresh and used catalyst.

The recycling experiments were performed to study the stability of Ru-WO_x/HZSM-5 catalyst (Figure S8). Based on the above results, the 5Ru-25WO_x/HZSM-5 catalyst exhibited ideal catalytic activity and was selected to investigate the stability under the reaction conditions (235 °C, 3 MPa H₂ and 10 h). It could be seen from Figure S8, at first run, the yields of ethanol and EG were 60.4% and 27.3%, respectively, and the catalytic activity slightly decreased with the catalyst being recycled. When the catalyst was run for four times, the yields of ethanol and EG decreased to 42.2% and 22.1%, respectively. Besides the poor stability of HZSM-5, the metal contents of fresh catalyst and used catalysts were also measured by ICP-AAS technology. The catalytic metals leaching test found 0.18% of Ru and 4.06% of W were lost (show in Table S3), which could also lead to the decrease of catalytic activity. Therefore, more work needs to be done to improve the stability of Ru-WO_x/HZSM-5 catalyst for the potential commercial application.