

Supplementary Information

The effect of physical morphology and chemical state of Ru on the catalytic properties of Ru-carbon for cellulose hydrolytic hydrogenation

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1 Materials

Nano-silica (10 ± 5 nm), cellulose (25 μ m), sorbitol, mannitol, ruthenium chloride (RuCl_3 , Ru 35~42%), oxalic acid, and zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were purchased from Shanghai Macklin Biochemical company. Isosorbide, ethylene glycol, glycerol, 1, 4-sorbitan, xylitol, sucrose, and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) were supported by Tianjin Kemiou Chemical Reagent company. All chemicals were analytical grade and used as received.

2 Zirconium phosphate (ZrP) preparation

ZrP was prepared as described by Weingarten et al.¹, which consisted of precipitation of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (100 mL, 1 mol/L) and $\text{NH}_4\text{H}_2\text{PO}_4$ (200 mL, 1 mol/L). The obtained white solid was filtered, washed with deionized water, and put in the oven at 100 °C for 12 h. Before use, the catalyst was powdered and calcined at 400 °C for 4 h.

3 Product analysis

After the reaction, the liquid products were filtrated and analyzed by HPLC (Waters e2695, 2414 refractive index (RI) detector and Asahipak column), and the results were quantified by an external standard method. The products, including isosorbide, ethylene glycol, glycerol, 1,4-sorbitan, xylitol, sorbitol, mannitol, and glucose were detected. The cellulose conversion and yield of each product were calculated as follows:

$$\text{Conversion (\%)} = \left(1 - \frac{W_{\text{unreacted cellulose}}}{W_{\text{charged cellulose}}} \right) \times 100\%$$

$$\text{Yield (\%)} = \frac{n_{\text{product}}}{n_{\text{cellulose}}} \times 100\%$$

Turnover frequency (TOF, h^{-1}) were determined using the equation below:

$$\text{TOF} = (n_{\text{cell.}} \times c_{\text{conv.}}) / (m \times l \times M \times t)$$

where $n_{\text{cell.}}$ is the initial mole of cellulose, mol. $c_{\text{conv.}}$ is the conversion of cellulose, %. m is the mass of catalyst in the reaction, g. l is the loading of Ru, %. M is the molar mass of Ru, g/mol. t is the reaction time, h.

4 The TGA of Ru/SiO₂@C

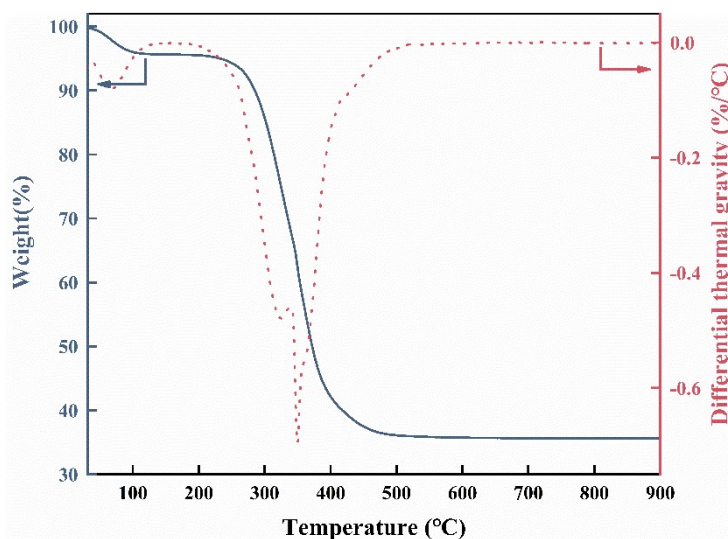


Fig. S1 The TGA image of Ru/SiO₂@C

The thermal decomposition of the catalyst precursor in the nitrogen atmosphere was studied by TGA, and the result was shown in **Fig. S1**. Two obvious stages of Ru/SiO₂@C appeared in the TG curve. The first 4% weight loss below 140 °C was caused by the loss of a small amount of physic-absorbed water². The second significant weight loss about 60% between 230 °C and 500 °C was ascribed to the decomposition of sucrose into CO₂ and water³.

5 The effect of carbonization temperature on the catalytic activity of Ru@MC

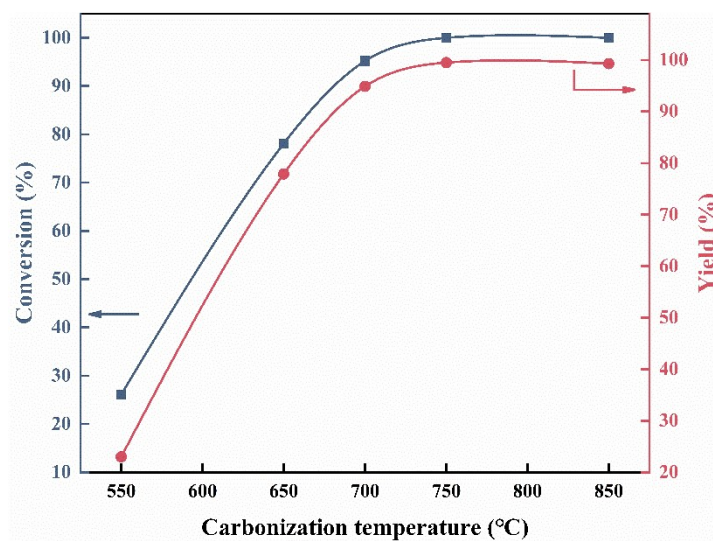


Fig. S2 The effect of carbonization temperature on the catalytic activity of Ru@MC

Reaction condition: 50 ml Glucose solution (0.1 mol/L), 80 mg Ru@MC, 120 °C, 2 MPa, and 2 h.

6 The effect of reaction condition on the cellulose conversion

The effect of Ru@MC amount on catalytic cellulose conversion was performed and the results were shown in **Fig. S3 (A)**. An increase of Ru@MC usage from 40 mg to 90 mg, the conversion of cellulose increased slightly from 59.6% to 75.1%; while the selectivity of sorbitol increased from 56.0% to 77.1% by elevating the dosage from 40 mg to 60 mg. Further increasing the dosage, the yield of sorbitol significantly reduced, owing to the hydrogenolysis reaction happened when the amount of Ru@MC was excessive. Thus, the optimal dosage of Ru@MC was 60 mg. The effect of reaction temperature on cellulose conversion was shown in **Fig. S3 (B)**. The conversion of cellulose increased slightly from 56.9% to 68.2% by increasing the H₂ pressure from 1 MPa to 6 MPa. With increasing H₂ pressure from 1 MPa to 5 MPa, the selectivity of sorbitol escalated from 55.6% to 77.4%. Further increasing the H₂ pressure, the selectivity of sorbitol began to decrease. The effect of reaction temperature on cellulose conversion was shown in **Fig. S3 (C)**. The result indicated that the cellulose conversion escalated significantly at first and then increased slightly with the increasing of temperature. When the temperature increased from 160 °C to 170 °C, the selectivity of sorbitol increased from 75.8% to 77.4%. Further increasing the temperature, the selectivity of sorbitol significantly decreased. The effect of reaction time on the conversion of cellulose was shown in **Fig. S3 (D)**. With increasing reaction time from 1 h to 2 h, the cellulose conversion and sorbitol selectivity escalated from 35.7% to 99.6% and 28.4% to 61.5%, respectively. Further prolonging the reaction time, the cellulose conversion remained unchanged, while the sorbitol yield began to decline. This result indicated that sorbitol would further be degraded into other undesired by-products when the reaction time was too long.

In summary, 61.5% of the sorbitol yield was obtained at the optimum reaction conditions of 170 °C, 3.5 h, and 60 mg Ru@MC.

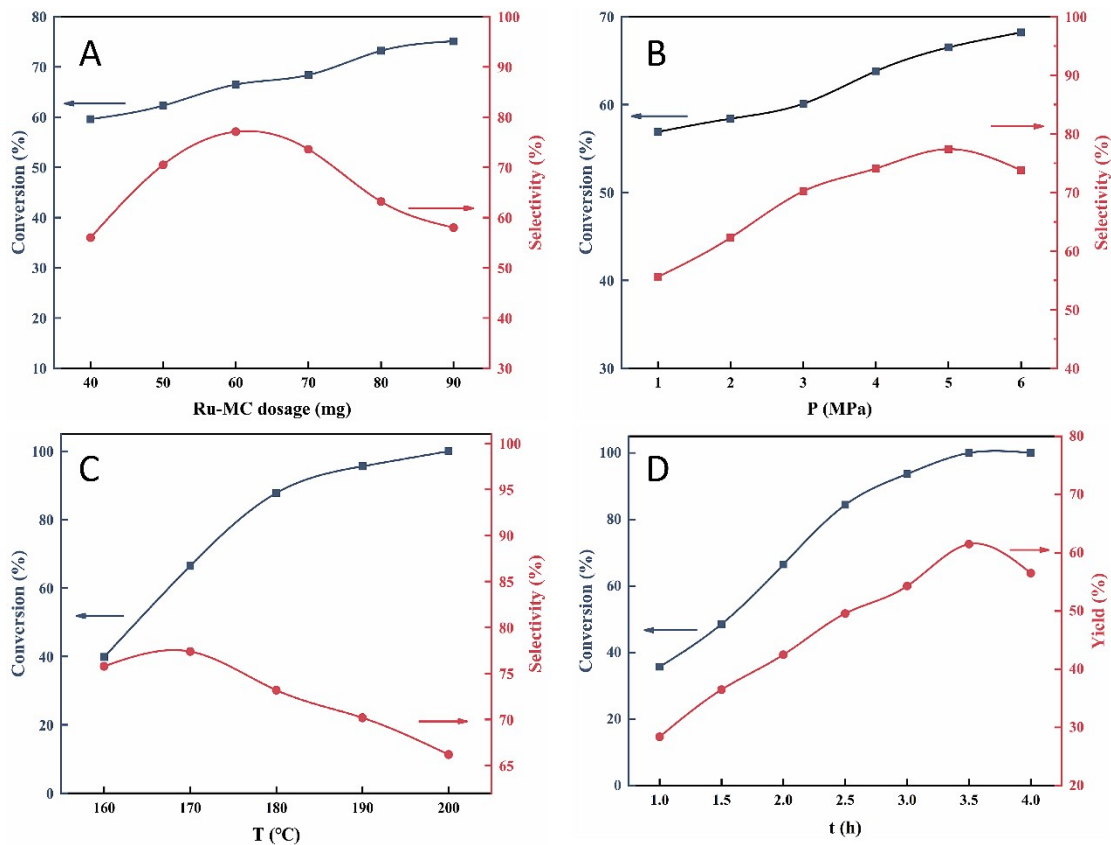


Fig. S3 The effect of reaction condition on the cellulose conversion.

Reaction condition: (A) Ru@MC dosage (170 °C, 5 MPa H₂, 2 h). (B) H₂ pressure (Ru@MC 60 mg, 170 °C, 2 h). (C) Temperature (Ru@MC 60 mg, 5MPa H₂, 2 h). (D) Reaction time (Ru@MC 60 mg, 170 °C, 5MPa H₂).

References

1. R. Weingarten, W. C. Conner, Jr. and G. W. Huber, *Energy & Environmental Science*, 2012, **5**, 7559-7574.
2. X.-Y. Liu, M. Huang, H.-L. Ma, Z.-Q. Zhang, J.-M. Gao, Y.-L. Zhu, X.-J. Han and X.-Y. Guo, *Molecules*, 2010, **15**, 7188-7196.
3. Q. Q. Zhou, X. Y. Chen and B. Wang, *Microporous and Mesoporous Materials*, 2012, **158**, 155-161.