Supplementary Information

Production of polyols from sugars in biorenewable alcohol: Selectivity of hydrogen transfer on metal catalysts

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This document contains 6 figures, 1 table, and 2 texts.

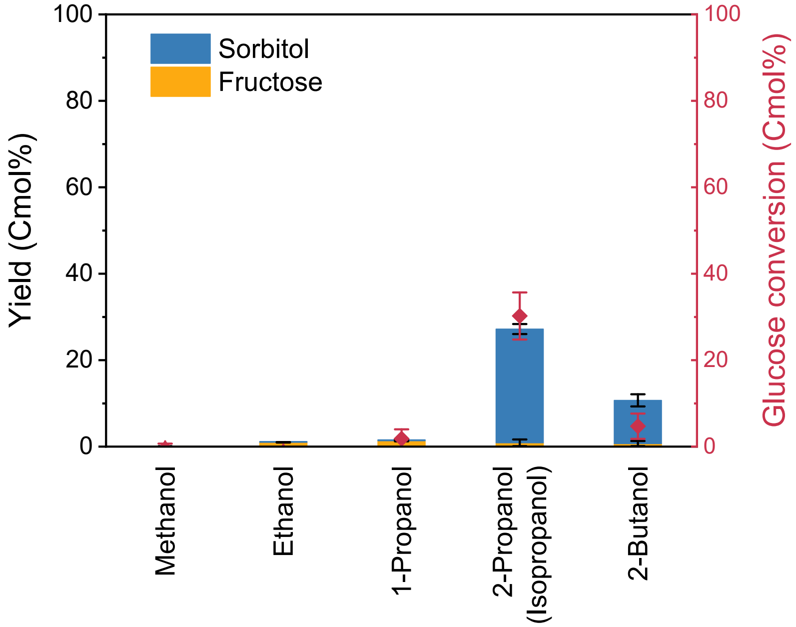


Figure S1. Glucose conversion and yields of fructose and sorbitol using various H donors for glucose CTH over pristine Ru/C catalyst (reaction conditions: 40 mg Ru/C, 40 mg glucose; solvent: 5 mL H donor and 5 mL water; 140°C, 30 min; Flexiwave).

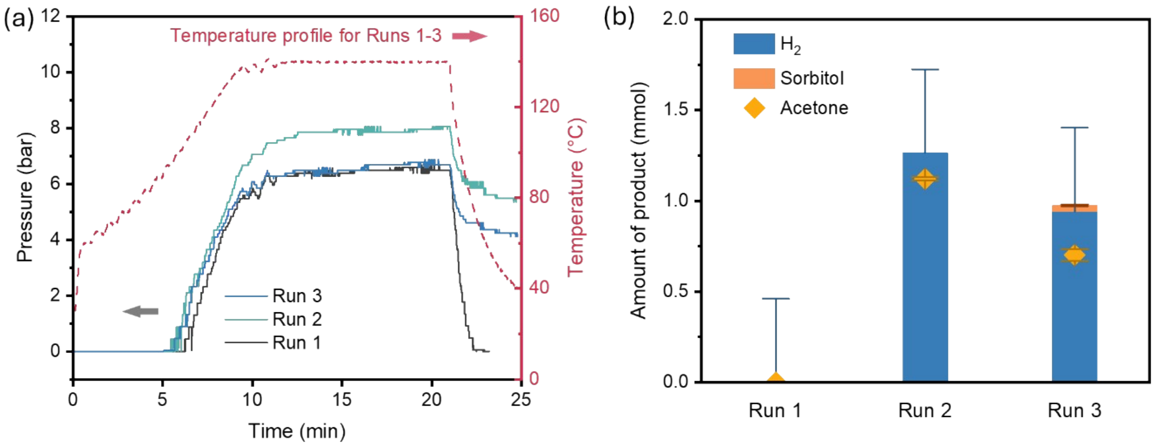


Figure S2. (a) Pressure and temperature profiles of solvent-only Run **1** (without catalyst or glucose), Run **2** with 16 mg Ru/C, and Run **3** with both 16 mg Ru/C and 16 mg glucose (solvent in all runs: 2 mL IPA and 2 mL water); (b) H balance after glucose CTH reaction – acetone amount indicates the donated H from IPA, while sorbitol amount represents the H utilized by glucose and H_2 amount (estimated based on post-reaction pressure after cooling down to 40°C using idea gas law) corresponds to the combined H (above runs conducted in Monowave 400, whose instrumental pressure error of ± 2 bar causing ± 0.46 mmol estimation error of H_2).

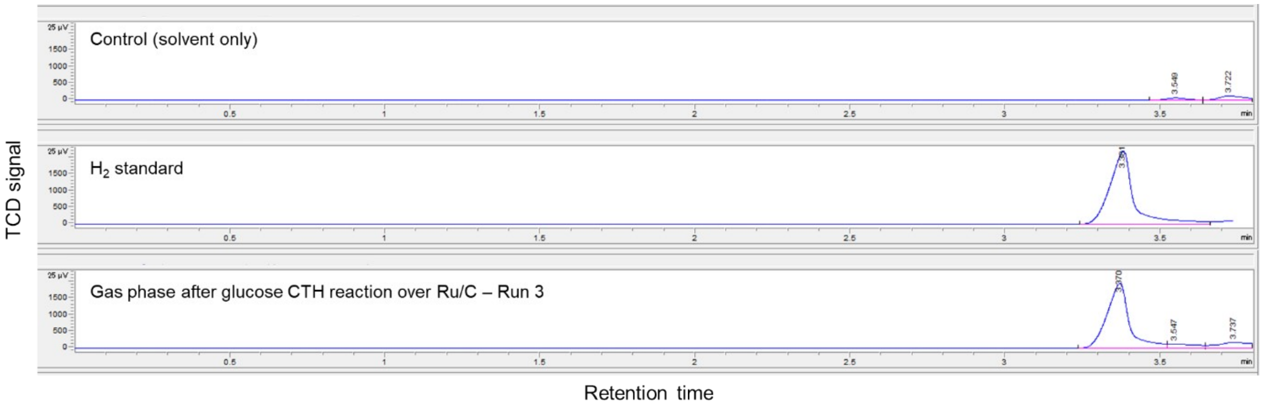


Figure S3. GC chromatogram of gas phase after glucose CTH reaction (16 mg glucose, 16 mg Ru/C, 2 mL IPA and 2 mL water; 140°C, 10 min; Monowave 400) with reference to the top gas of solvent-only control and H_2 standard.

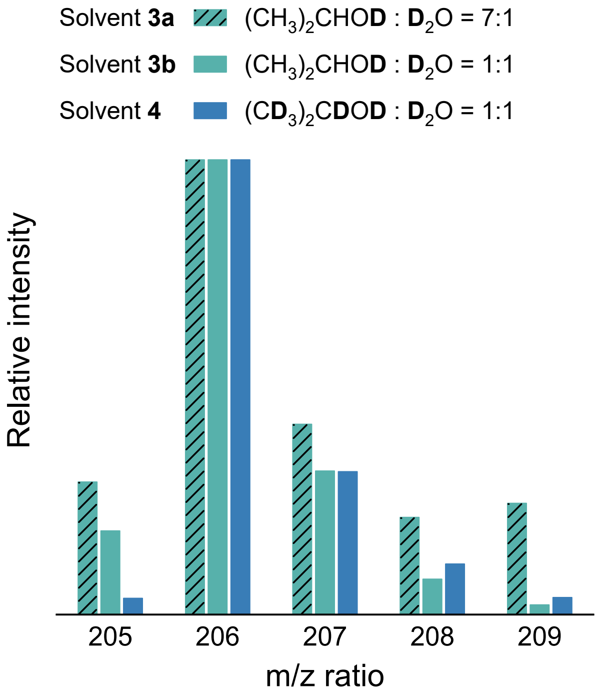


Figure S4. ESI-MS profile of products from glucose CTH in various D-labelled solvents with low and high water contents (Reaction conditions: 16 mg glucose, 16 mg Ru/C, 4 mL total volume of solvent; 140 °C, 10 min; Monowave 400. Assignment of main adducts: m/z 205 for $[C_6H_{14}O_6+Na]^+$, m/z 206 for $[C_6H_{13}DO_6+Na]^+$, and m/z 207 for $[C_6H_{12}D_2O_6+Na]^+$).

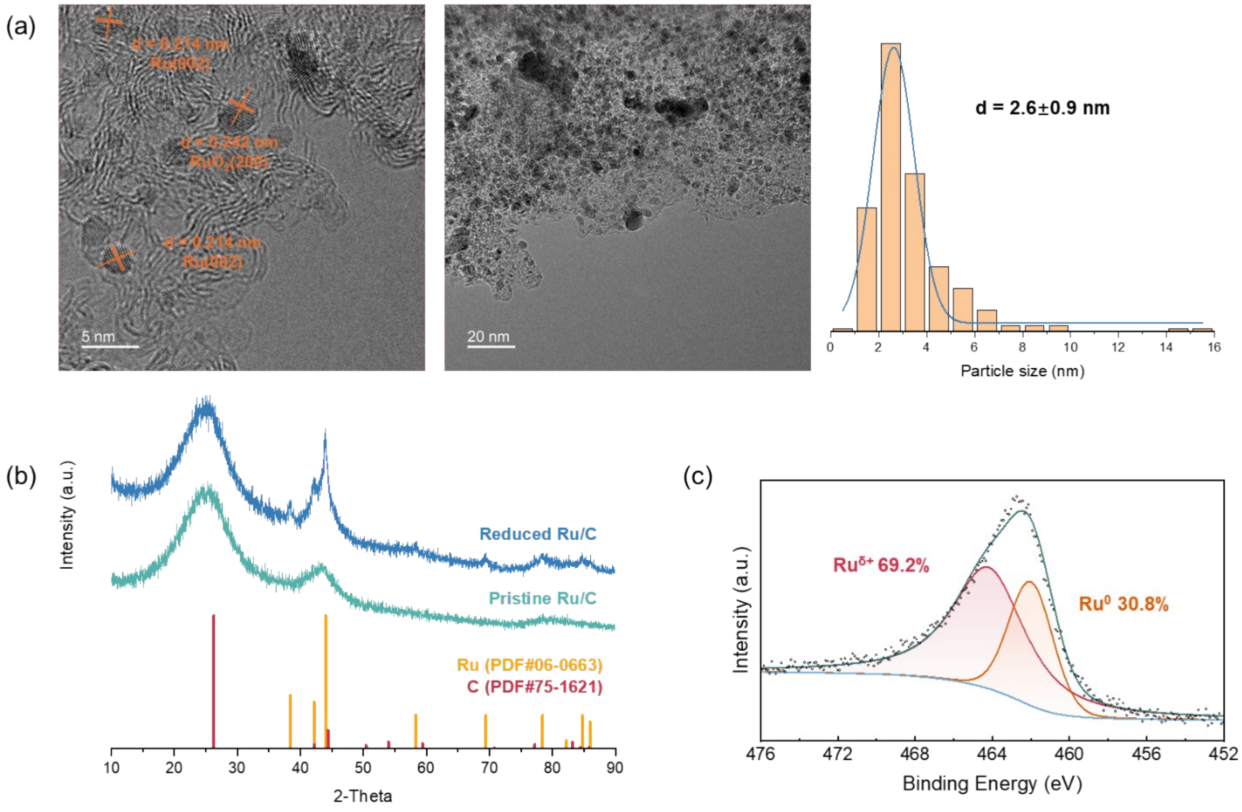


Figure S5. Characterization of reduced Ru/C: (a) TEM images with typical lattice spacing (Ru PDF#06-0663 and RuO_2 PDF#50-1428) and particle size distribution; (b) XRD patterns with peak references; and (c) deconvoluted Ru 3p XPS spectra.

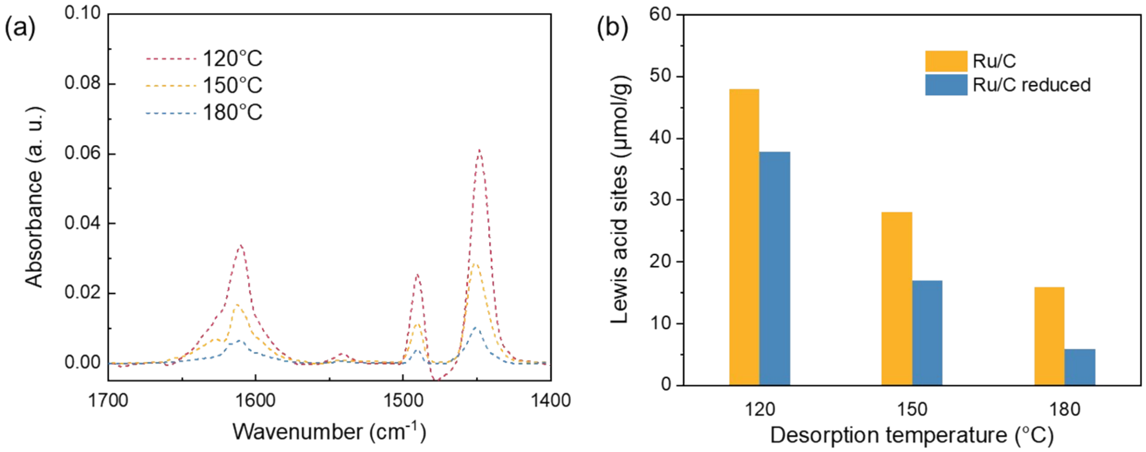


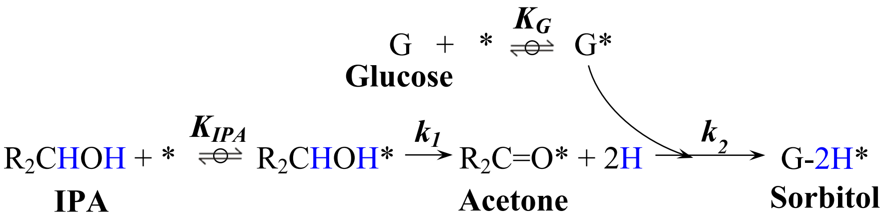
Figure S6. Pyridine-FTIR spectra of (a) reduced Ru/C at various pyridine desorption temperatures, and (b) Lewis acid site concentrations of pristine and reduced Ru/C quantified based on the spectra shown in (a).

Table S1. Comparison with reported catalytic performance of Ru-based catalyst for the CTH of glucose and representative biomass-derived molecules.

Catalyst	**Substrate**	**H donor and solvent**	**Reaction conditions**	**Catalytic performance**	**Ref.**
2%Ru supported on N-doped ordered mesoporous carbon (CMK-1), 10 mg	Glucose 45 mM	IPA 2 mL, water 2 mL	Temperature 170°C, Time 3 h, P(N_2) 15 bar	Glucose conversion 100 %, sorbitol yield 99.58 %	[1]
Ru(II) complexes of aminomethylphosphine ligands supported on Fe_3O_4@SiO_2 (core@shell), 100 mg	Glucose 1 mmol	IPA 10 mL, water 15 mL, K_2CO_3 0.1 mmol	Temperature 150°C (microwave), Time 40 min	Glucose conversion 99.11 %, sorbitol yield ~96.3 %	[2]
2%Ru supported on activated charcoal powder, 100 mg	Glucose 324 mg	IPA 20 mL, water 20 mL	Temperature 180°C, Time 20 min, P(Ar) 15 bar (at room temperature)	Glucose conversion 82 %, sorbitol yield ~76%	[3]
5%Ru supported on carbon, 100 mg	5-(hydroxymethyl)furfural (HMF) 240 mg	IPA 24 mL	Temperature 150°C, Time 6 h, P(N_2) 20.4 bar	HMF conversion ~80% 2,5-bis(hydroxymethyl)furan (BHMF) yield 38%	[4]
5%Ru supported on carbon, 100 mg	Furfural 1 wt%	IPA 24 mL	Temperature 180°C, Time 10 h, P(N_2) 20.4 bar	Furfural conversion 95%, fufural alcohol yield ~1%, methyl furan yield 61%	[5]
3%Ru supported on mesoporous $NiAl_2O_4$ materials, 80 mg	Guaiacol 0.167 g	IPA 4 mL, water 6 mL	Temperature 200°C, Time 2 h, P(Ar) 7 bar	Guaiacol conversion 86.54 %, cyclohexanol yield 63.98 %	[6]
5%Ru supported on carbon, 16 mg	Glucose 16 mg	IPA 2 mL, water 2 mL	Temperature 140°C (microwave), Time 20 min	Glucose conversion 87.5 %, sorbitol yield 82.8 %	This study

Text S1. Establishment of kinetic model (1)

A Langmuir-Hinshelwood model is considered for the studied heterogeneous catalytic system:



Scheme S1. Reaction network for glucose CTH with IPA as the H donor. $\boldsymbol{K_G}$ – equilibrium constant of glucose adsorption; $\boldsymbol{K_{IPA}}$ – equilibrium constant of IPA adsorption; $\boldsymbol{k_1}$ – rate constant of IPA dehydrogenation; $\boldsymbol{k_2}$ – rate constant of H addition to glucose to form sorbitol.

Considering the balance of the coverages (θ) of empty site (*), glucose (G), and IPA:

$$\theta_* + \theta_G + \theta_{IPA} = 1$$ (Eqn. S1)

Assumption: both IPA and glucose are adsorbed on the same site, i.e., Ru^0 (competitive adsorption).

Considering the adsorption equilibrium constants according to Langmuir equation:

$$K_G = \frac{\theta_G}{C_G\theta_*}$$ $\theta_G = K_G C_G \theta_*$ (Eqn. S2a)

$$K_{IPA} = \frac{\theta_{IPA}}{C_{IPA}\theta_*}$$ $\theta_{IPA} = K_{IPA} C_{IPA} \theta_*$ (Eqn. S2b)

Substituting Eqn. S2a and S2b into the coverage balance (Eqn. S1):

$$\theta_* + K_G C_G \theta_* + K_{IPA} C_{IPA} \theta_* = 1$$

$$\theta_* = \frac{1}{1 + K_G C_G + K_{IPA} C_{IPA}}$$ (Eqn. S3)

Substituting Eqn. S3 into Eqn. S2a and S2b:

$$\theta_G = \frac{K_G C_G}{1 + K_G C_G + K_{IPA} C_{IPA}} \tag{Eqn. S4a}$$

$$\theta_{IPA} = \frac{K_{IPA} C_{IPA}}{1 + K_G C_G + K_{IPA} C_{IPA}} \tag{Eqn. S4b}$$

The rate of IPA dehydrogenation (denoted as r_1) as well as the rate of sorbitol formation (r_2) can be expressed as follows:

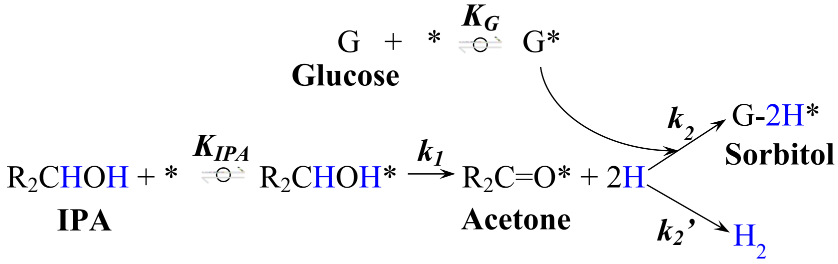
$r_1 = k_1 \theta_{IPA}$

$r_1 = r_2$

$$r_1 = r_2 = \frac{k_1 K_{IPA} C_{IPA}}{1 + K_G C_G + K_{IPA} C_{IPA}} \tag{Eqn. S5}$$

Text S2. Establishment of kinetic model (2).

This model is adapted from model (1) described in **Text S1**, considering combination of *H atoms as a competitive path in parallel with H* addition to glucose. As both models (1) and (2) share the same quasi-equilibrated steps, **Eqn. S1-4** that describes coverages and equilibrium constants apply in both models.



Scheme S2. Reaction network for glucose CTH with IPA as the H donor. $\boldsymbol{K_G}$ – equilibrium constant of glucose adsorption; $\boldsymbol{K_{IPA}}$ – equilibrium constant of IPA adsorption; $\boldsymbol{k_1}$ – rate constant of IPA dehydrogenation; $\boldsymbol{k_2}$ – rate constant of H addition to glucose to form sorbitol; $\boldsymbol{k_2}$**'** – rate constant of H-H combination into H_2.

Since sorbitol formation (rate denoted as r_2) and H_2 formation (rate denoted as $r_2^{'}$) are parallel, competitive steps, the following relationship applies:

$$r_1 = r_2 + r_2^{'}$$

$$r_2^{'} = r_1 - r_2 \qquad \text{(Eqn. S6)}$$

The rate equations for r_2 and $r_2^{'}$ and their ratio:

$$r_2 = k_2\theta_G\theta_H^2$$

$$r_2^{'} = k_2^{'}\theta_H^2$$

$$\frac{r_2}{r_2^{'}} = \frac{k_2\theta_G\theta_H^2}{k_2^{'}\theta_H^2} = \frac{k_2\theta_G}{k_2^{'}} \qquad \text{(Eqn. S7)}$$

Substituting Eqn. S6 into S7:

$$\frac{r_2}{r_1 - r_2} = \frac{k_2\theta_G}{k_2^{'}}$$

$$r_2 k_2^{'} = r_1 k_2 \theta_G - r_2 k_2 \theta_G$$

$$r_2 (k_2^{'} + k_2\theta_G) = r_1 k_2 \theta_G$$

$$r_2 = \frac{r_1 k_2 \theta_G}{k_2^{'} + k_2 \theta_G} \qquad \text{(Eqn. S8)}$$

References

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