# Supporting Information

# Bimetallic ruthenium-copper nanoparticles embedded in mesoporous carbon as an effective hydrogenation catalyst

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## 1. Catalytic conversion of D-glucose and selectivity of sorbitol

Prior to the first hydrogenation batch, we use the RuC catalyst to do the preliminary reaction.[1] Fig. S1 shows the concentration profiles of D-glucose and sorbitol as a function of hydrogenation time. It can be seen that the initial rate of the D-glucose consumption was not significantly fast. Instead, after 2h, the conversion rate of D-glucose became faster than the first 2h. After 3h, the conversion rate became very slow. Thus we set the reaction time as 3h for all the catalysts to compare their catalytic performance. Fig. S2 shows the high-performance liquid chromatography (HPLC) profiles of diluted product solution with RuC, RuCu0.5C, and CuC as catalysts, respectively. The HPLC spectrum showed that sorbitol was the only product in the presence of all the catalysts. Thus, the selectivity of sorbitol was 100%. Therefore, we use the mean catalytic activity, which was calculated as the yield of moles of sorbitol per mole of Ru per second, to compare the performance of all the catalysts.[2]
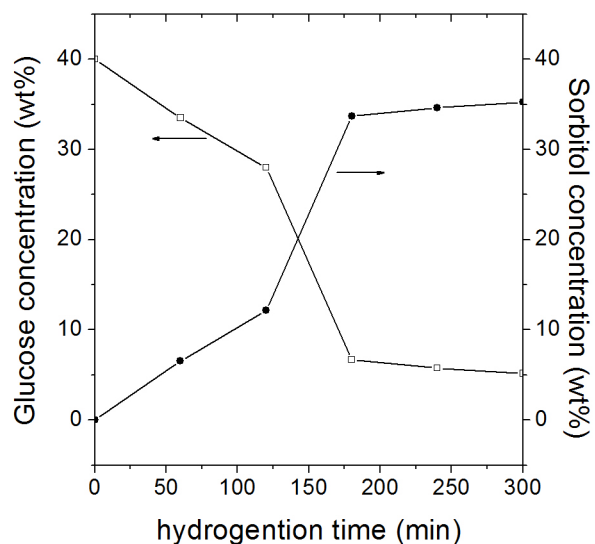
Fig. S1. Typical concentration profile of the hydrogenation of D-glucose to sorbitol (RuC, 8MPa, 100 °C, 40 wt% glucose).
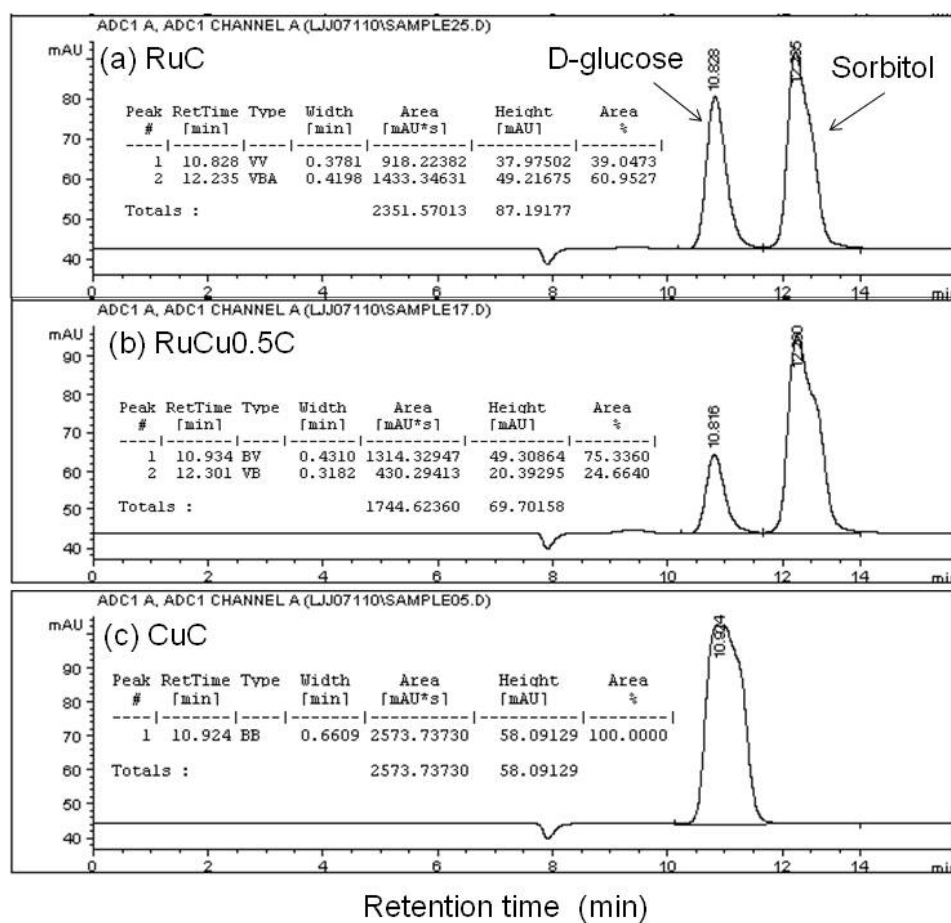


Fig. S2. HPLC spectrum of the diluted product solution with (a) RuC, (b) RuCu0.5C, (c) CuC as catalysts, respectively.

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## 2. Kinetics of the hydrogenation of D-glucose

The D-glucose hydrogenation experiments were carried out in a batch Parr Reactor (Parr 4560) operating at 4-10 MPa and between 90 and 120 $^{o}$C. The effect of stirring rate was studied in the beginning of the work, in order to eliminate the mass transfer limitation. The affection on initial reaction rate by changing the stirrer speed from 300 rpm to 1500 rpm was shown in Fig. S3. The stirring speed was fixed at 1000 rpm for the experiments to ensure that the gas-liquid mass transfer does not affect the reaction rate. Aqueous solutions contained about 20-50 wt% glucose initially. The liquid volume was 30 ml and the amount of catalyst RuCu0.5C was 0.05 g. The average catalyst particle length is 15μm. The initial rate $r_0$ was obtained by recording the drop of $H_2$ pressure with time, which was then transferred into the hydrogen uptake rate per square meter of Ru (mol·min$^{-1}$·m$^{-2}$) according to the ideal gas equation and the active surface area (calculated by $H_2$ chemisorption). The influence of the catalyst loading was evaluated by varying the catalyst-to-glucose ratio in D-glucose hydrogenation experiments at 100 $^{o}$C and 8MPa. The initial reaction rate showed a linear dependency on the catalyst load between 0.03 and 0.1 g, i.e. the normalized activity was independent of the catalyst loading, indicating that in the range of operating variables the systems is not controlled by gas-liquid mass transport (Fig. S3b). Nevertheless, a further increase of the catalyst loading did not give a full benefit.
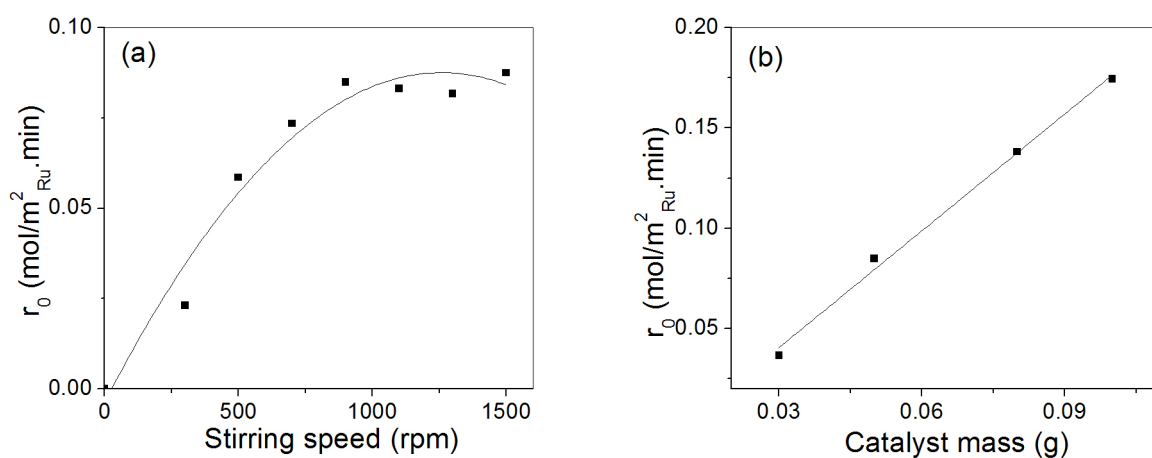


Fig. S3 (a) Effect of the stirring speed on the initial reaction rate at 100 $^{o}$C and 8MPa, (b) The influence of catalyst loading on the initial reaction rate at 100 $^{o}$C and 8MPa.

From the experiments carried out at the temperature range at 90-120 $^{\circ}$C and at pressure 4-10 MPa, it was found that the apparent activation energy for D-glucose hydrogenation over RuCu0.5C was 49.7-66.4 kJ/mol (Fig. S4). The estimated activation energies were much larger than the activation energy of diffusion in liquids (12-21 kJ/mol),[3] thus indicating that the experiments were performed under kinetics control.
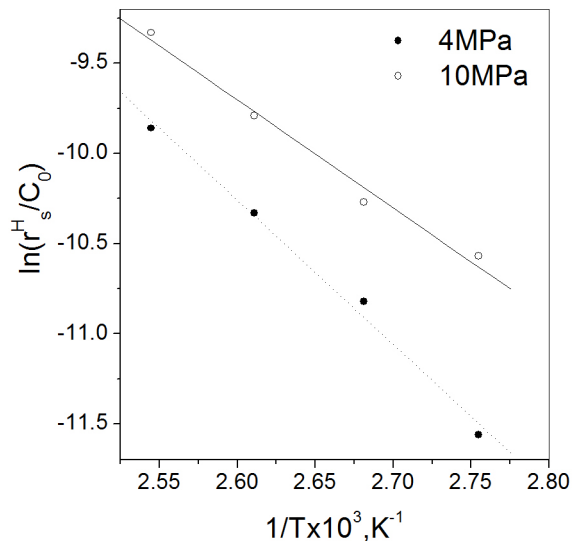


Fig. S4 Arrhenius plots of the initial glucose (40wt% in water) hydrogenation rates carried out at 4 MPa ($E_a$=66.4 kJ/mol) and 10 MPa ($E_a$=49.7 kJ/mol) and at the temperature range 90-120 $^{\circ}$C.

The dependency of initial reaction rate on initial D-glucose concentration at 100 $^{\circ}$C was plotted in Fig. S5a. This figure would well agree with a classical Langmuir-Hinshelwood model, in which the products and the solvent are not involved in the rate expression:

$$r_0 = \frac{k K_G C_{G0}}{1 + K_G C_{G0}} \tag{S1}$$

At low D-glucose concentration (< 40 wt%), apparent first order kinetics was observed. At high D-glucose concentration ($\geq$ 40 wt%), saturation of the catalyst surface occurred and zero order was observed.
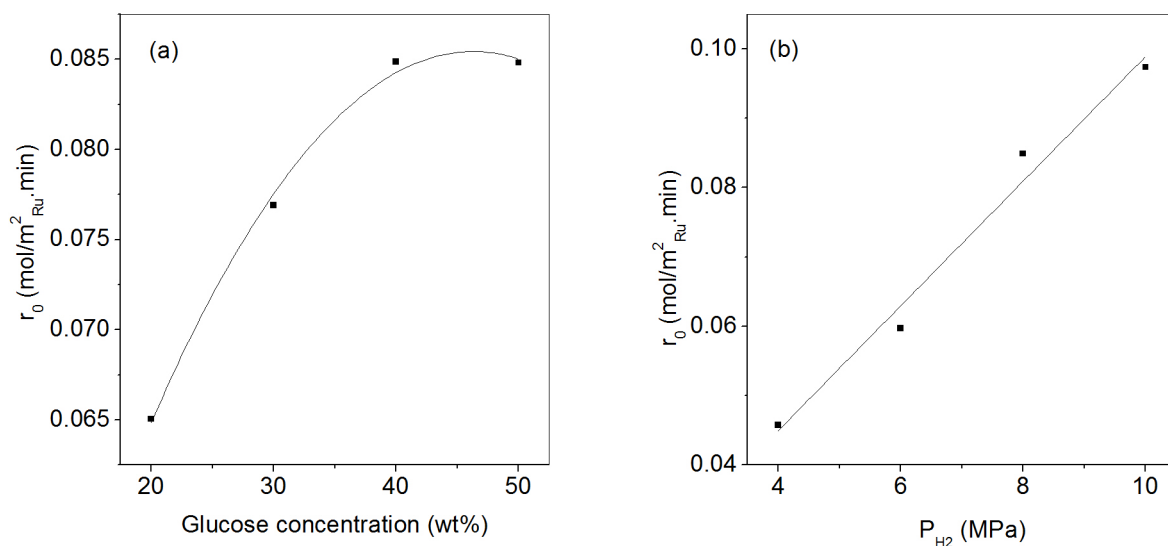
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Fig. S5 (a) D-glucose concentration dependency of the initial hydrogenation rate at 100 $^{\circ}$C, 0.05g catalyst, 8 MPa; (b) initial D-glucose hydrogenation rate as a function of hydrogen pressure at 100 $^{\circ}$C, $C_{G0}$=40wt%, 0.05 g catalyst.

An increased hydrogen pressure had a positive effect on the initial reaction rate, showing first order behavior at 100 $^{\circ}$C (Fig. S5b). The kinetic behavior in Fig. S5b could be understood by considering the difference in the adsorption strength between D-glucose and hydrogen on RuCu0.5C catalysts. As the D-glucose molecule was strongly adsorbed, it reached to saturated adsorption rapidly. Thus, the change in the D-glucose concentration in the liquid phase did not change its adsorption amount on the catalyst and thus, did not affect the rate of the surface hydrogenation. The adsorption of hydrogen on RuCu0.5C was relatively weak and could not reach saturated adsorption under the present reaction conditions. Therefore, the initial rate exhibited first-order with respect to hydrogen pressure.

**Modeling results of kinetics and mechanism**

Based on preliminary kinetics analysis, some simplifications can be made: i) no catalyst deactivation occurred during the reaction; ii) the reaction is 100% selective to D-sorbitol; iii) there is negligible adsorption of solvent and D-sorbitol; iv) the adsorption and desorption steps are assumed to be rapid, whereas the hydrogenation steps on the surface are presumed to be rate controlling; v) the

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hydrogenation steps are regarded as irreversible; vi) hydrogen adsorption was assumed to be dissociative, but hydrogen atoms were supposed to be added pairwise to the organic species.

As a summary, the complete set of plausible surface steps is presented below:

$$H_2 + 2^* \leftrightarrow 2\,(H^*)$$

$$G + {}^* \leftrightarrow G^*$$

$$G^* + 2\,(H^*) \rightarrow S + 3^*$$
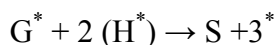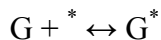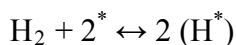
It has previously been proposed that sugar hydrogenation follow a competitive adsorption model, where adsorbed atomic hydrogen is added pairwise to adsorbed organics. However, because of the larger size of difference between sugar molecules and hydrogen, another non-competitive adsorption model was assumed, where hydrogen and D-glucose adsorbed at different sites.[4-6] As a result, two models based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) were used. Model 1: non-competitive adsorption of dissociatively chemisorbed hydrogen and D-glucose at different sites, see Eq. (S2); Model 2: competitive adsorption of dissociatively chemisorbed hydrogen and D-glucose, see Eq. (S3).

$$r = \frac{k_r K_G C_G K_H P_{H_2}}{1 + K_G C_G} \tag{S2}$$

$$r = \frac{k_r K_G C_G K_H P_{H_2}}{\left(1 + K_G C_G\right)^3} \tag{S3}$$

The temperature dependencies of $k_r$, $K_G$ and $K_H$ are:

$$k_r = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{S4}$$

$$K_G = \exp\left(\frac{-\Delta H_G}{RT} + \frac{\Delta S_G}{R}\right) \tag{S5}$$

$$K_H = \exp\left(\frac{-\Delta H_H}{RT} + \frac{\Delta S_H}{R}\right) \tag{S6}$$

Since $k_r$ and $K_H$ only appear as a product in the rate expressions, it was expressed as $k_r K_H$.

$$k_r K_H = k_0 \exp\left(\frac{\Delta S_H}{R}\right) \exp\left(\frac{-(E_a + \Delta H_H)}{RT}\right) \tag{S7}$$

The experiments performed at 100 °C were used to obtain the parameters $k_r K_H$ and $K_G$ at this temperature. The fit of the experimental data to the kinetic model was carried out by Matlab software by fminsearch method (generally referred to as unconstrained nonlinear optimization). The results of parameter estimation are summarized in Table S1. Fig. S6 illustrates that the Model 2 nicely described the behavior of the system.

Table S1 Comparison of the fitted parameters for D-glucose hydrogenation over RuCu0.5C catalyst.

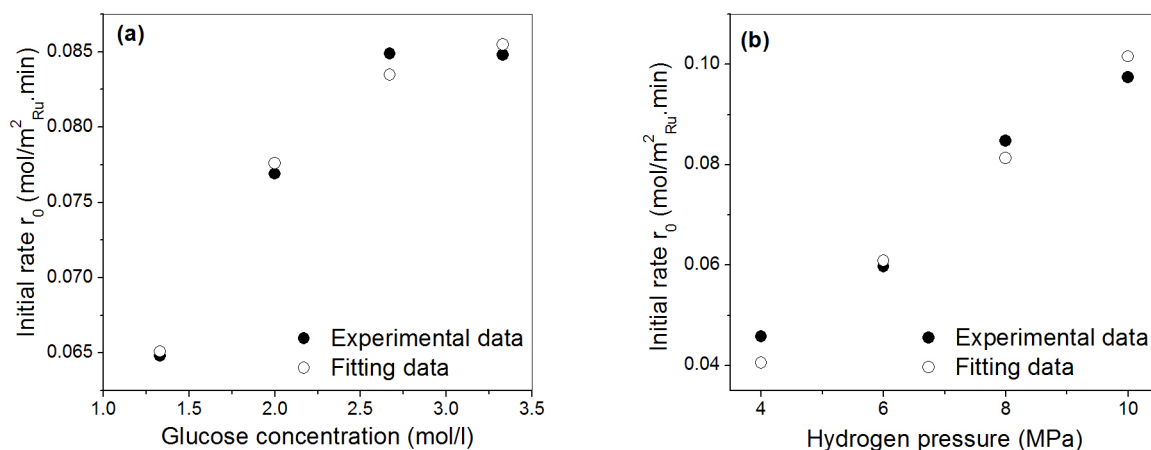| | Model 1 | Model 2 |
|---|---|---|
| $k_r K_H$ (mol/(min·m²$_{Ru}$·MPa)) | 0.0137 | 0.0722 |
| $K_G$ (l/mol) | 1.1398 | 0.1427 |
| Sum of squares of residuals (SSR) | $5.7665 \times 10^{-4}$ | $4.8929 \times 10^{-4}$ |



Fig. S6 Fit of kinetic model 2 to experimental data for hydrogenation of D-glucose over RuCu0.5C.

Therefore, based on the literature review and the kinetic data, we proposed that the hydrogenation of D-glucose over RuCuC involves the formation of an ionized glucose species adsorbed on the Ru or Cu surface by coordination of O-1, O-5, and O-6, which was then polarized, and attacked by a hydride-like species from the Ru surface or the spillover hydrogen atom from Ru to Cu (see Fig. S7). The adsorptions of dissociatively chemisorbed hydrogen and D-glucose are competitive.
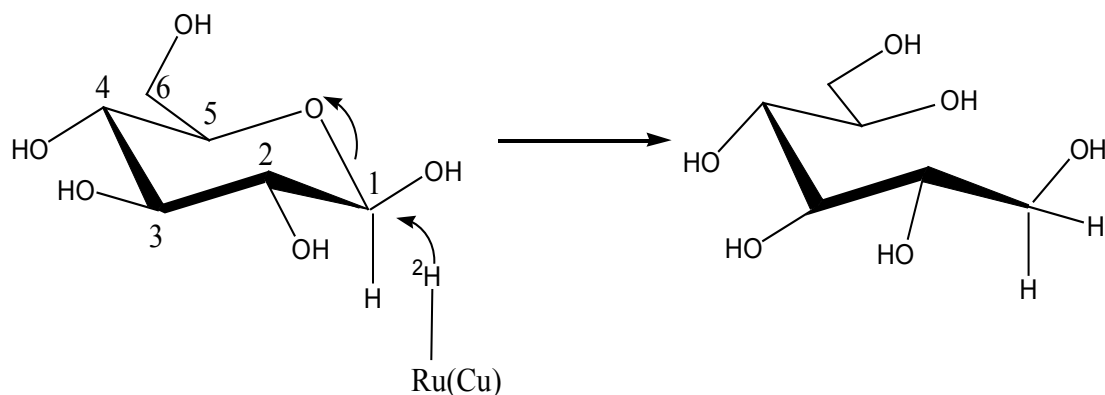
Fig. S7 Schematic representation of the reaction mechanism between adsorbed β-D-glucopyranose and hydrogen.

Reference

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