

## Electronic Supporting Information

### Homologous RuO<sub>2</sub>-Ru heterostructures for tandem catalytic upgrading of ethanol

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## **Experimental section:**

### **Synthesis of biomass-derived porous carbon**

The biomass-derived porous carbon support was synthesized via a modified hard-template method. Firstly, aluminum nitrate nonahydrate (48 g), citric acid (13.5 g), and sucrose (15.6 g) were mixed together in a three-neck flask, in which 200 mL of deionized water was added to form a homogeneous mixture. Then, 8.7 mL of phosphoric acid (85%) was added dropwise into the above solution. After standing for 0.5 h, a dilute alkali aqueous solution (10 wt% ammonia) was used to slowly adjust the pH value of the solution to 5.1. Afterward, the as-made mixture was heated at 80 °C in the open air to remove the water and other volatiles. The resultant solid was ground into black powder, treated at 300 °C in muffle for 10 minutes, and then calcined at 800 °C under an Ar flow for 6 h. The biomass-derived porous carbon (denoted as C) was obtained after etching of AlPO component by excess 4 M HNO<sub>3</sub>.

### **Synthesis of catalysts**

The RuO<sub>2</sub>-Ru/C catalysts were prepared by an impregnation method using C as the support. Firstly, different amounts of the RuCl<sub>3</sub>·3H<sub>2</sub>O were dissolved in a certain amount of deionized water under continuous stirring. Next, the C support was added and dispersed by stirring for 3 h under room temperature to ensure uniform distribution. The obtained mixture was dried at 80 °C using a water bath under stirring. The resulting material was calcinated at 400 °C for 4 h in Ar atmosphere. The RuO<sub>2</sub>-Ru/C samples synthesized in this work were denoted as x wt%RuO<sub>2</sub>-Ru/C (x = 0.2, 0.5, 1.0 and 2.0), where x is the Ru loading in weight percent ( $x = [\text{Ru/C}]_{\text{wt}} \times 100\%$ ).

The actual Ru contents for 0.2 wt%RuO<sub>2</sub>-Ru/C, 0.5 wt%RuO<sub>2</sub>-Ru/C, 1.0 wt%RuO<sub>2</sub>-Ru/C and 2.0 wt%RuO<sub>2</sub>-Ru/C are 0.15 wt%, 0.4 wt%, 0.75 wt% and 1.5 wt%, respectively.

Pt/C (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O as a metal precursor, calcined in Ar at 300 °C for 2h), Pd/C (PdCl<sub>2</sub> as a metal precursor, calcined in Ar at 300 °C for 2h), and Cu/C (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O as a metal precursor, calcined in Ar at 450 °C for 4h) were synthesized following a similar procedure to RuO<sub>2</sub>-Ru/C.

### Catalyst Evaluation

The catalytic test was carried out using a fixed-bed reactor. In detail, a given amount of catalyst (1.0 g) was loaded into the tubular reactor. Subsequently, the ethanol and carrier gas nitrogen (N<sub>2</sub>) was fed from the top of the reactor. The reaction was carried out under the following conditions: 523 K, 2 MPa, LHSV = 3.6 mL·h<sup>-1</sup>·g<sub>cat</sub><sup>-1</sup> and N<sub>2</sub> flowing rate = 35 mL·min<sup>-1</sup>. The liquid products were analyzed by a Gas chromatograph (GC) with a flame ionization detector (FID) and a SE-54 column (30 m, 0.25 mm inner diameter).

The ethanol conversion, selectivity and yield of products were calculated as follows:

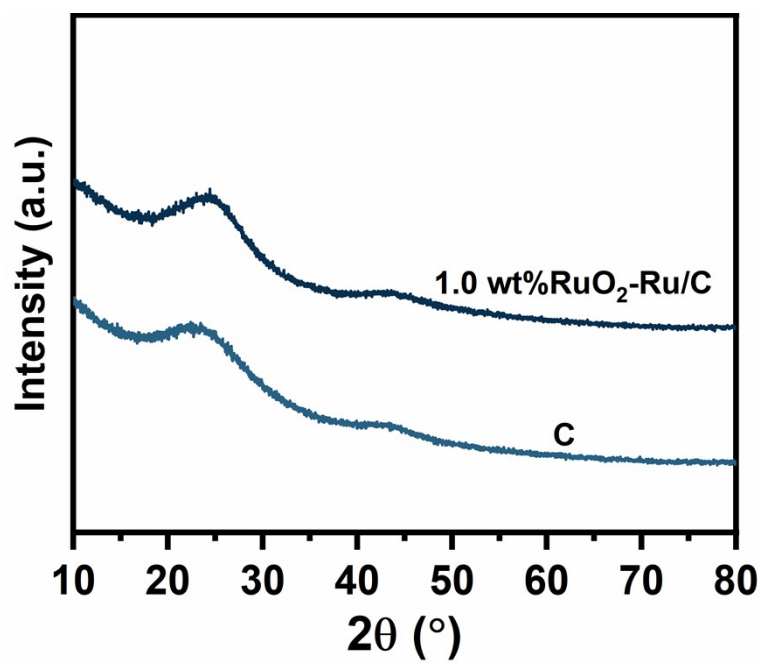
$$\begin{aligned} \text{Ethanol conversion (\%)} &= \frac{x \text{ mol of carbon in all products}}{x \text{ mol of carbon in (all products + unreacted ethanol)}} \times 100\% \\ \text{Selectivity (\%)} &= \frac{x \text{ mol of carbon in the target product}}{x \text{ mol of carbon in all products}} \times 100\% \end{aligned}$$

$$\text{yield (\%)} = \text{Ethanol conversion} \times \text{Selectivity}$$

### Characterizations

The crystal phases were examined by XRD using a Rigaku X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ = 0.15418 nm), operated at 40 kV and 40 mA. N<sub>2</sub>-

adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 analyzer. TEM and HAADF-STEM images were obtained on a JEOL JEM-2100F instrument with an operating voltage of 200 kV. X-ray photoelectron spectroscopy characterization was conducted on a Thermo Nexsa instrument with an Al K $\alpha$  source (1486.6 eV). Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed with a Agilent 725 instrument. Hydrogen-temperature programmed desorption (H<sub>2</sub>-TPR) performed using a ChemBET Pulsar TPR/TPD instrument. Before detection, the samples were pretreated under N<sub>2</sub> flow at 300 °C for 30 min. After cooling to 30 °C, the flowing gas was switched to a 5 vol% H<sub>2</sub>/Ar and the sample was heated to 800 °C with a ramp of 10 °C/min.



**Fig. S1** XRD patterns of the carbon support and 1.0 wt% RuO<sub>2</sub>-Ru/C.

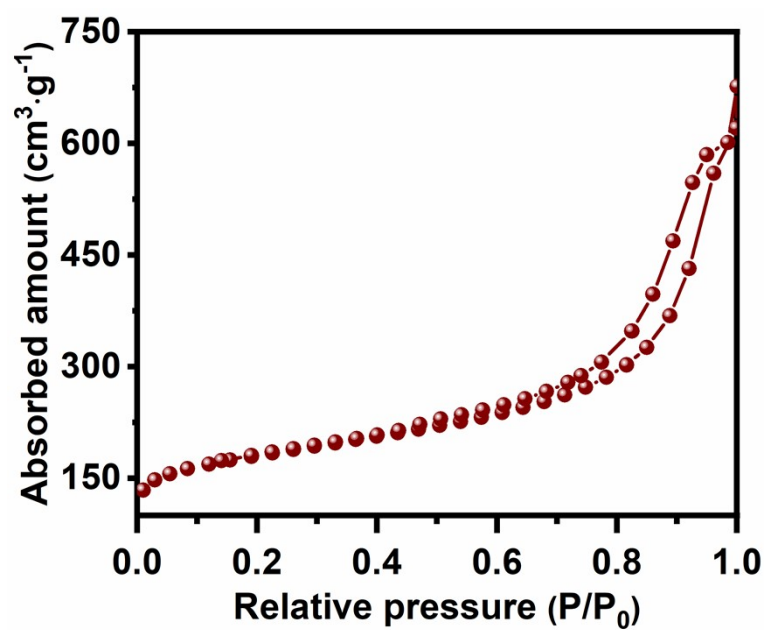


Fig. S2 N<sub>2</sub> adsorption-desorption isotherms of 1.0 wt% RuO<sub>2</sub>-Ru/C.

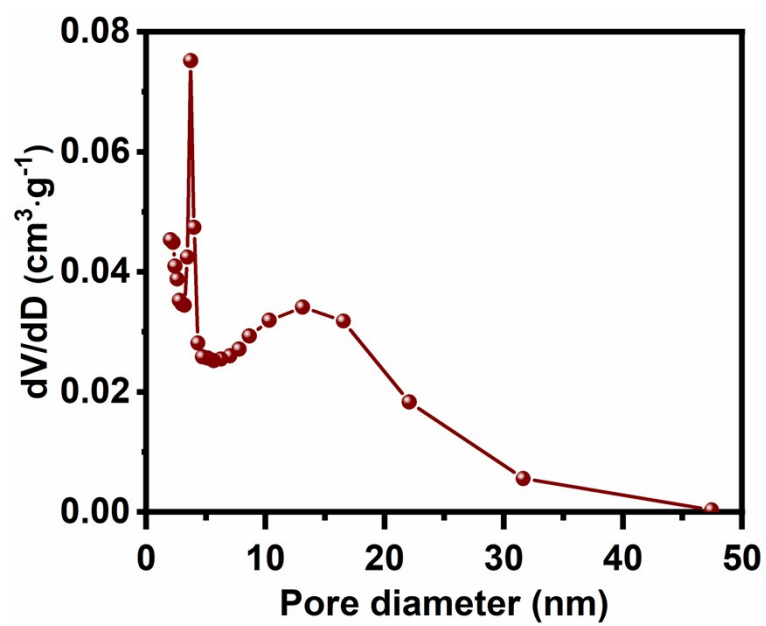
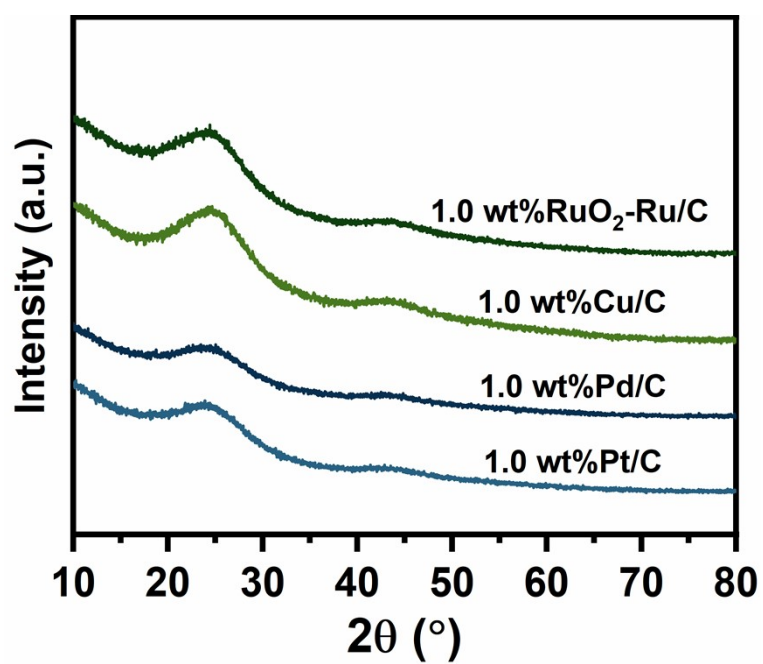


Fig. S3 BJH pore size distribution of 1.0 wt% RuO<sub>2</sub>-Ru/C.



**Fig. S4** XRD patterns of 1.0 wt% Pt/C, 1.0 wt% Pd/C, 1.0 wt% Cu/C and 1.0 wt% RuO<sub>2</sub>-Ru/C.



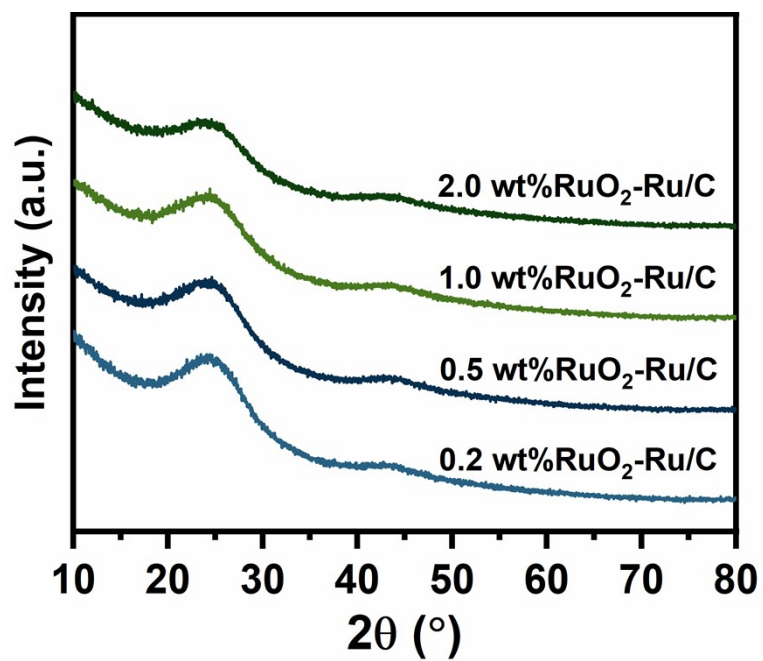
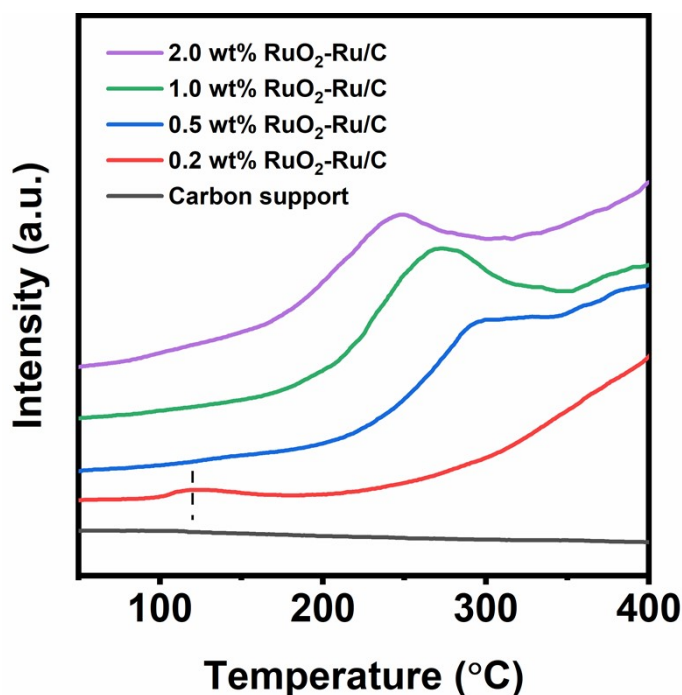
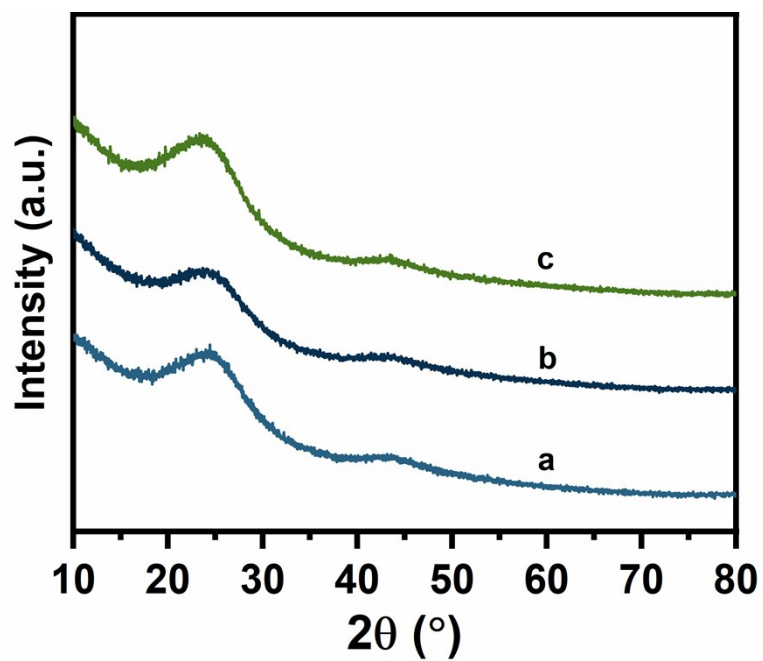


Fig. S5 XRD patterns of RuO<sub>2</sub>-Ru/C with different Ru loadings.

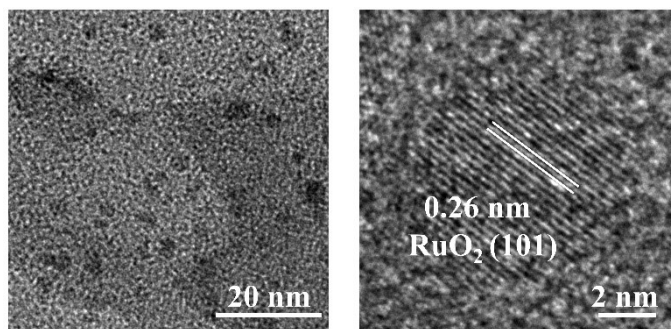


**Fig. S6** H<sub>2</sub>-TPR profiles of carbon support and RuO<sub>2</sub>-Ru/C with different Ru loadings.

The H<sub>2</sub>-TPR profiles of RuO<sub>2</sub>-Ru/C catalysts with Ru loading of 0.5-2.0 wt% exhibit a predominant peak at 180-350 °C, corresponding to the reduction of RuO<sub>2</sub> to metallic Ru. The reduction peak gradually shifts to relatively low temperature with the Ru content increasing, probably because the Ru species with low loading has a stronger interaction with support. For 0.2 wt% RuO<sub>2</sub>-Ru/C, the reduction peak located at 120 °C, which is lower than the RuO<sub>2</sub>-Ru/C catalysts with Ru loading of 0.5-2.0 wt%, mainly due to the small particle size. In addition, considering the H<sub>2</sub> consumption and Ru loading, we can conclude that the ratio of RuO<sub>2</sub> to Ru increased with Ru loading from 0.2 to 1.0 wt %, but it declined as Ru loading was raised to 2.0 wt%.



**Fig. S7** XRD patterns of 1.0 wt% RuO<sub>2</sub>-Ru/C before reaction (a) and after the initial change (b) and long-term reaction (c).



**Fig. S8** TEM and HRTEM images of used RuO<sub>2</sub>-Ru/C.