Supporting information for

Strong Metal Support Interaction in Ru/V_2O_3 Mitigates Reactant Induced Poisoning during Succinic Acid Hydrogenation

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Detailed experimental procedures

Procedure for STEM/TEM

A tiny amount of sample was dispersed in anhydrous ethanol via sonication. The sample was then drop casted to the grids (grid names) and vacuum dried before measurement.

Nitrogen physisorption

The powdered samples were outgassed at 150 °C for 2 hours under dynamic vacuum prior to the measurement. Physisorption measurements were then performed at -196 °C with a BELSORP mini automatic analyzer. Surface areas were determined using Brunauer-Emmet-Teller equation from the 0.05 to 0.35 relative pressure region of the isotherms.[47]

Calculation of metal dispersion from STEM

The metal dispersion was calculated form STEM images using the following equation by Bergeret and Gallezot[48] –

$$Dispersion(\%) = \frac{6 \times \left(\frac{V_m}{a_m}\right)}{d_p} \times 100$$

where V_m in nm^3 represents volume occupied by an atom in bulk metal, a_m in nm^2 represents area occupied by a surface atom and d_p in nm represents surface averaged particle size measured form STEM. Where, d_p was calculated using the following equation –

$$d_p = \frac{\sum d^3}{\sum d^2}$$

Where d is particle sizes calculated from STEM images.

Table S1. Metal dispersion calculated from STEM images.

Reduction temperature	Dispersion (%)
200	81
300	72
400	51
500	31

Procedure for XPS

The powdered samples were reduced at desired temperature according to the procedure mentioned in catalyst synthesis method, in a glass tube, which was then opened in a glovebox. The powdered samples were loaded in a double sided copper tape and the sample were introduced the measurement chamber without exposure to atmosphere.

CO chemisorption

CO chemisorption was done in pulse mode at 50 °C in BELCAT II instrument with thermal conductivity detector (TCD). The sample was reduced at desired temperature before the experiment.1 minute pulses of 5 % CO was injected in intervals until saturation of peak area corresponding to one pulse.

Procedure for the HD exchange reactions

HD exchange reactions were carried out BELCAT II instrument with a BELMASS II ms detector. 40 mg sample was used for the measurement. The program used for the experiments is given in **Figure S11**.

Procedure for temperature programmed reduction experiments

Temperature programmed reduction (TPR) of the unreduced catalyst were conducted using a BELCAT II instrument with a TCD detector. 40 mg sample was used for the measurement. Prior the measurement, the sample was pretreated at 200 °C under 30 $mLmin^{-1}$ Ar flow to remove any excess moisture or physisorbed species. Measurements were done at a flow rate of 50 $mLmin^{-1}$ of 2.5 % H_2-Ar mixture with a temperature ramp rate of 10 °C min^{-1}. In case of physical mixture of sample and WO_3, 40 mg sample and 160 mg WO_3 was taken.

In Situ IR studies

For In Situ IR measurement about 40 mg of catalyst was pressed into a 1.3 mm diameter self-supporting disk. The disk was placed in a quartz IR cell fitted with NaCl window, capable of heating as shown in **Figure S1.** The sample was first reduced at desired temperature with the flow of 30 mL/min He and 10 mL/min H_2 for 30 minutes, after which the H_2 flow was stopped, and the cell was cooled to 150 °C. After the temperature was stable, sample spectra was collected as background and then 10 mL/min D_2 flowed through the system and spectra was recorded every minute (2 scans) for 30 minutes.

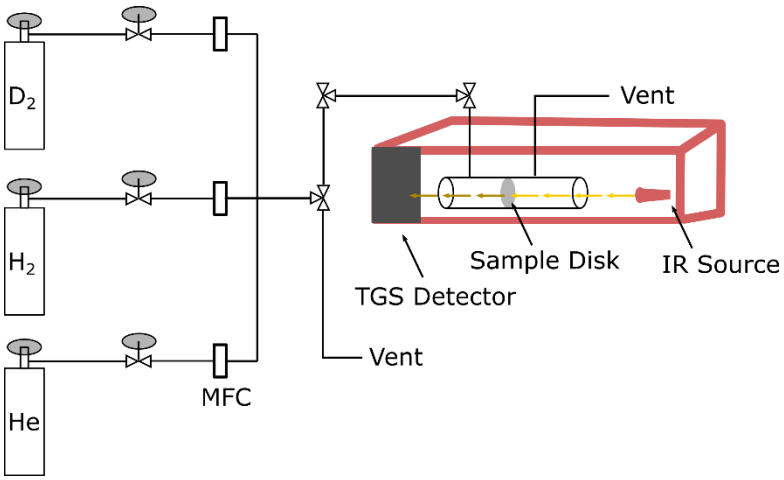

Figure S1.Schematic diagram of the in situ IR system.

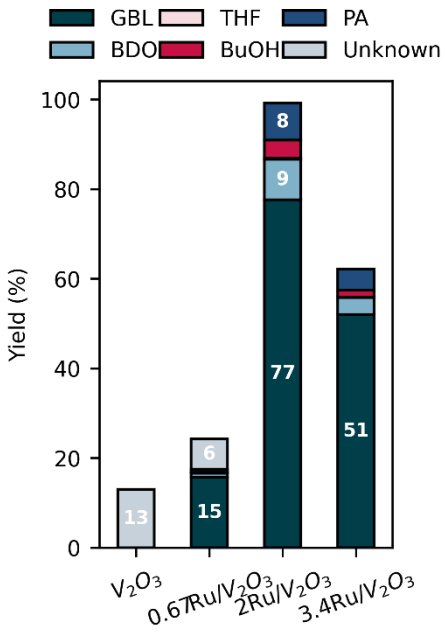

Figure S2. Optimization of ruthenium loading keeping reduction temperature fixed at 400 °C. Reaction conditions: succinic acid 0.118 g (1 mmol), catalyst 0.05 g, H_2 5 MPa, 150 °C, 6 h. Unknown in the figure represents difference between succinic acid conversion and total yield of detected products, total height of the bars represent total conversion..

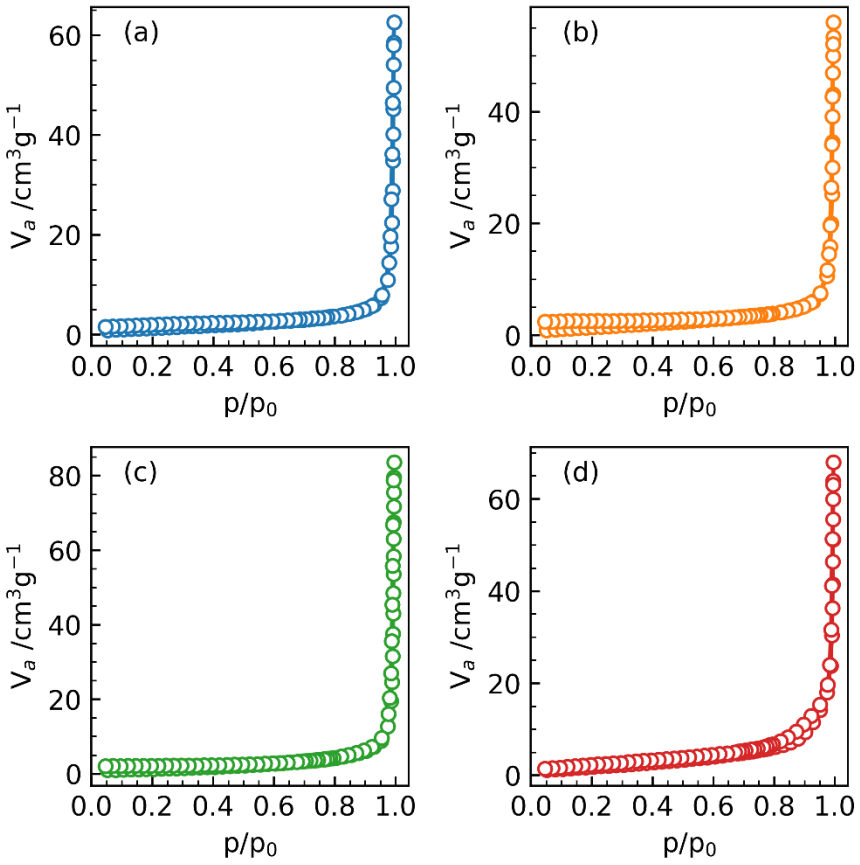

Figure S3. N_2-sorption isotherm of Ru/V_2O_3 catalysts used reduced at (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.

Table S2. Surface area of Ru/V_2O_3 catalysts reduced at different temperatures.

Catalyst	Surface Area (m^2g)
Ru/V_2O_3-200	5.6
Ru/V_2O_3-300	5.0
Ru/V_2O_3-400	4.8
Ru/V_2O_3-500	4.7

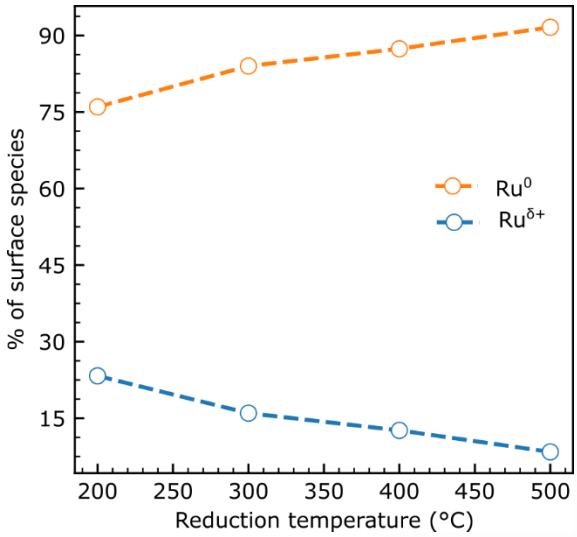

Figure S4. Variation of percentage of surface metallic and surface oxidic ruthenium species with reduction temperature.

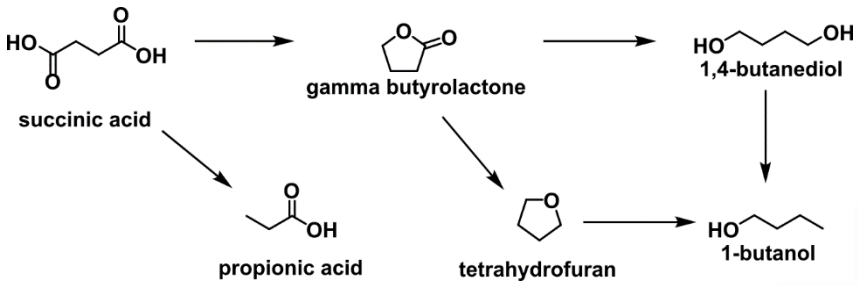

Figure S5. Reaction pathway for conversion for succinic acid to gamma butyrolactone.

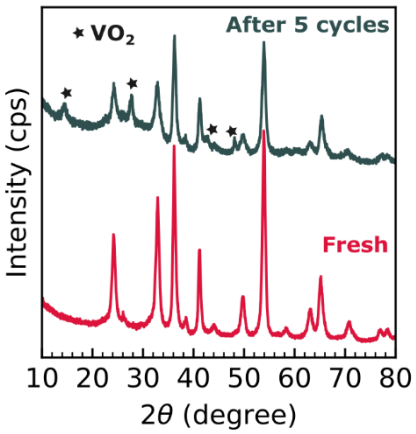

Figure S6. Succinic acid hydrogenation over Ru/V_2O_3 at different hydrogen pressures. reaction conditions – succinic acid 0.118 g (1 mmol), catalyst 0.05 g, H_2 5 MPa, 150 °C, 6 h. Unknown represents difference between succinic acid conversion and total yield of detected products, total height of the bars represent total conversion.

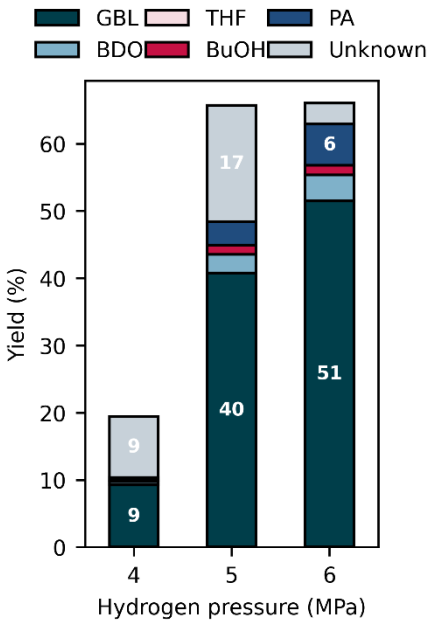

Figure S7. Succinic acid hydrogenation over Ru/V_2O_3 at different hydrogen pressures. reaction conditions – succinic acid 0.118 g (1 mmol), catalyst 0.05 g, H_2 5 MPa, 150 °C, 6 h. Unknown represents difference between succinic acid conversion and total yield of detected products, total height of the bars represent total conversion.

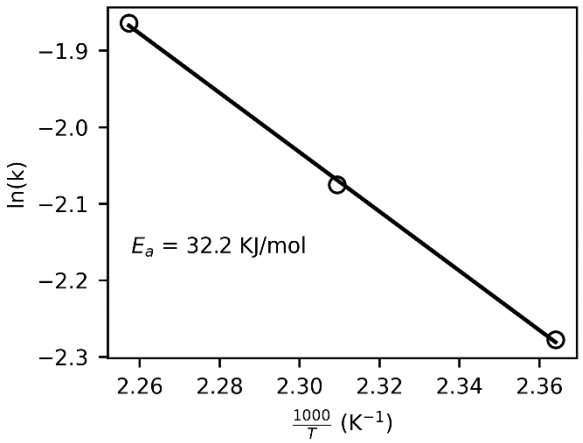

Figure S8. Arrhenius plot for succinic acid hydrogenation over Ru/V_2O_3-400 catalyst. Reaction conditions – succinic acid 0.118 g (1 mmol), catalyst 0.05 g, H_2 5 MPa, 150 – 170 °C, 6 h.

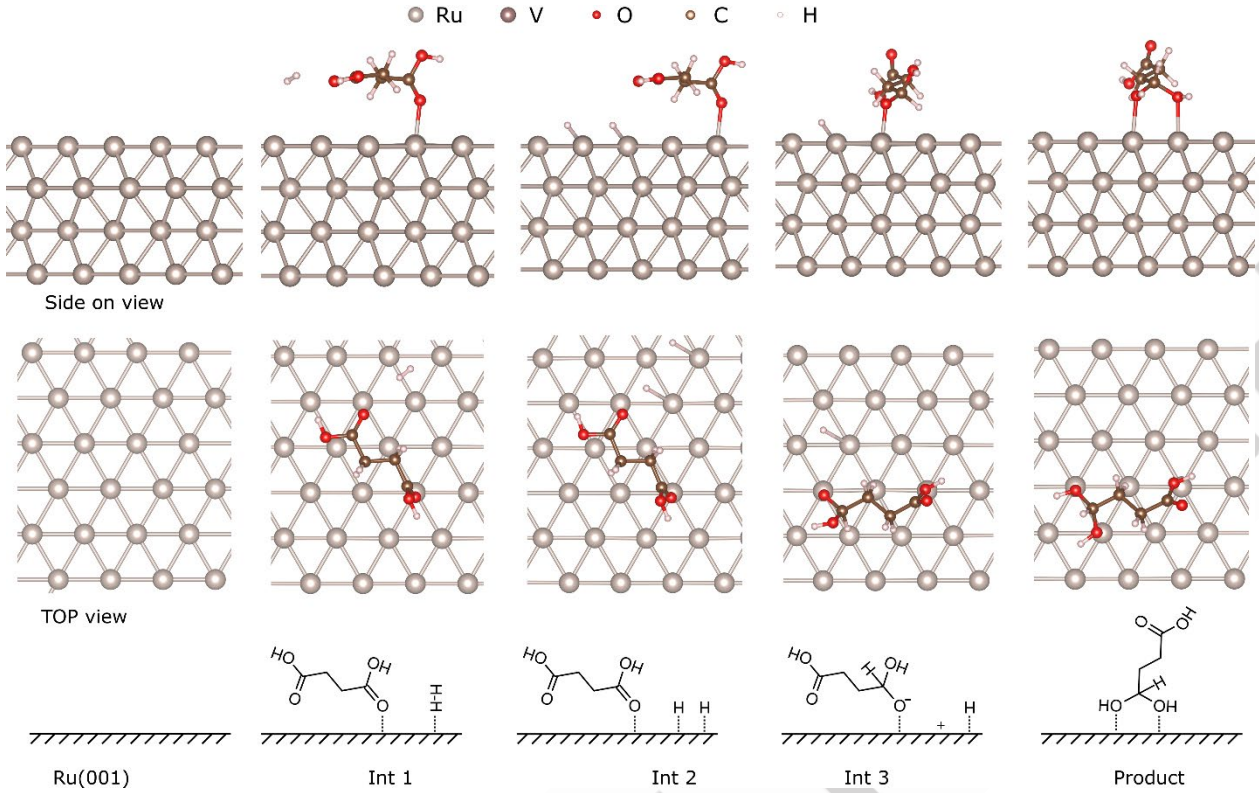

Figure S9. Side view and Top view of the intermediates at bare Ru (001) surface.

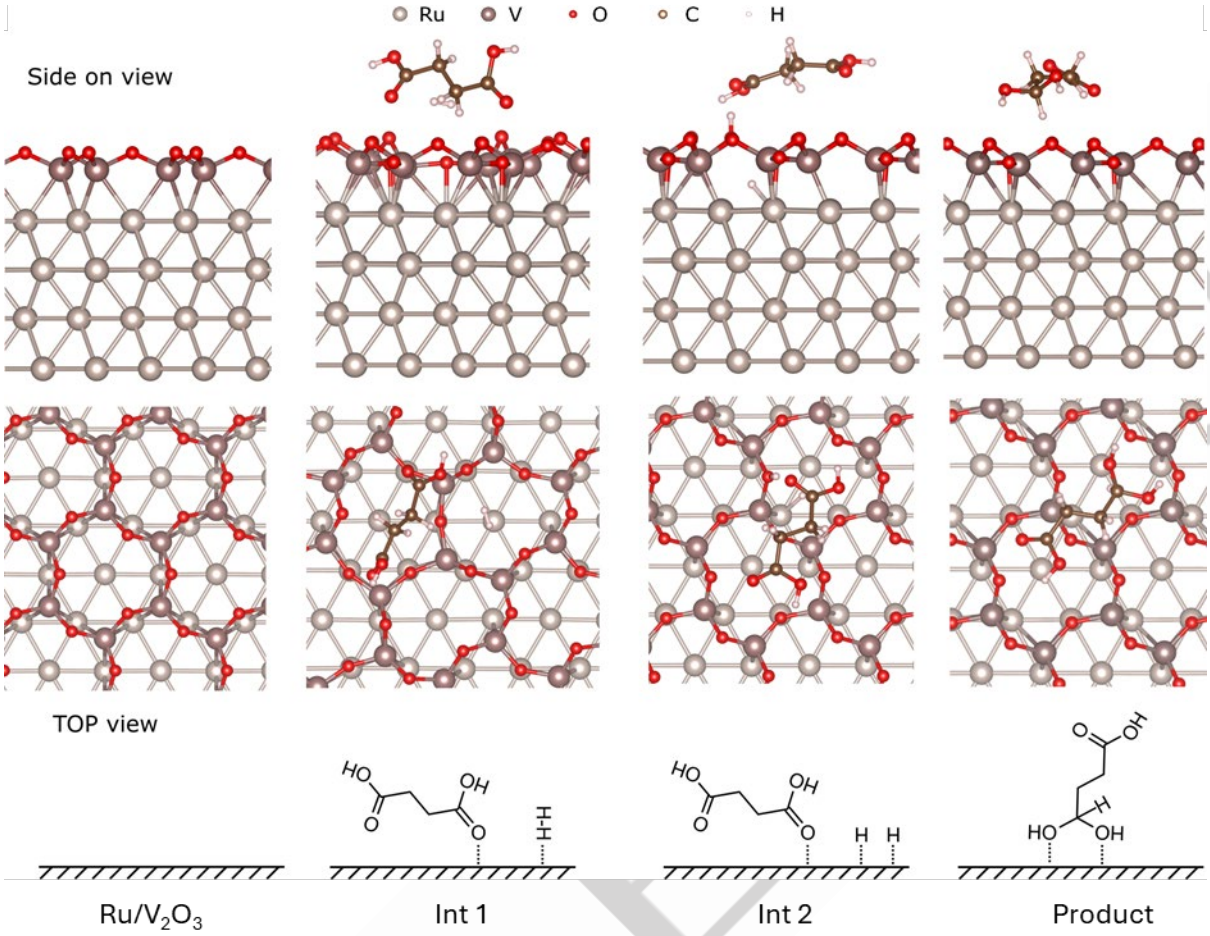

Figure S10. Side on view and top view of the intermediates on Ru/V_2O_3 surface.

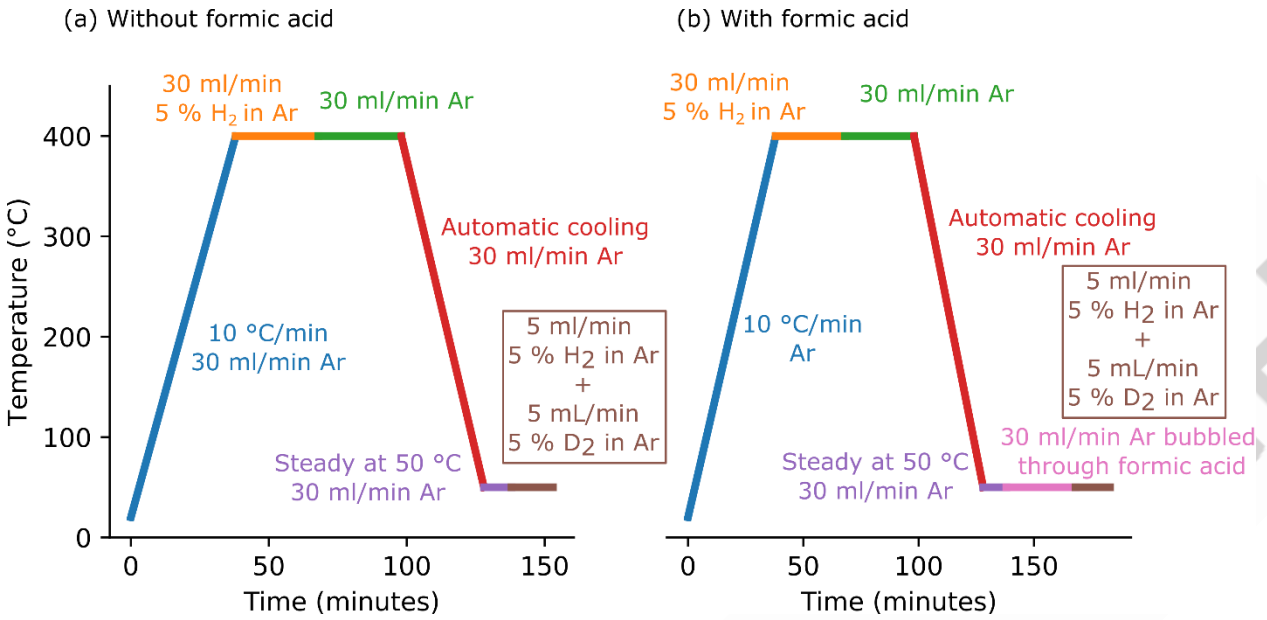

Figure S11. Procedure for HD exchange reaction on the Ru/V_2O_3 400 (a) without formic acid, (b) with formic acid.

References

[47] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
[48] G. Bergeret, P. Gallezot, in *Handb. Heterog. Catal.* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley, **2008**, pp. 738–765.