

Supporting information

Ethylene carbonylation to 3-Pentanone with in-situ hydrogen via water-gas-shift reaction on Rh/CeO₂

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Experimental section

1. Catalyst Preparation

CeO₂ nanoparticles were prepared through a conventional precipitation method. Typically, 15 g Ce(NO₃)₃·6H₂O was dissolved in 300 mL DI water. Then ammonia solution was added dropwise to the cerium solution to obtain Ce(OH)₃, with the pH value of the resulting solution controlled at around 11. After stirring overnight, the precipitate was washed by filtration. The solid was dried at 70 °C overnight and then calcined at 500 °C for 4 h in muffle furnace. The Rh/CeO₂ was prepared by wet impregnation method using RhCl₃·3H₂O as the Rh source: firstly, 2g CeO₂ nanoparticles was added to an aqueous solution containing certain amount of Rhodium(III) chloride trihydrate. After stirring overnight, the suspension was dried at 120 °C under stirring. The solid was calcined at 200 °C for 4 h under air atmosphere and then reduced at 200 °C for 4 h in a tube-furnace with H₂. Other oxides supported metal catalysts were prepared via the same procedure and all the metal contents were 1 wt %.

2. Characterization

HRTEM:

Dark field scanning transmission electron microscopy (DF-STEM) images were acquired on a Hitachi HF5000 at Ernst Ruska Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute (Forschungszentrum Juelich GmbH, Juelich, Germany). The electron microscope was operated at 200 kV, which is a cold FEG TEM/STEM with a Cs probe corrector. Compositional maps were obtained by energy-dispersive X-ray spectroscopy (EDX) analysis using double EDX Ultra 100 detector from Oxford Instruments.

Raman spectroscopy:

Raman spectra were measured on a Renishaw Company spectrograph with spectral resolution of 2 cm⁻¹. The laser line at 532 nm of a solid laser was used as the exciting source and the power of the laser, measured at the samples, was about 0.3 mW.

Py-IR:

Self-supporting wafers (10-20 mg/cm²) were pressed and sealed in an IR heatable cell. The sample was reduced with H₂ at 200 °C for 0.5 h and cooled to 30 °C under dynamic vacuum. At this point, a baseline spectrum was recorded. Then pyridine was introduced and spectra were acquired after the cell was evacuated under dynamic vacuum for every 20 min. To study the water adsorption, water was introduced into the IR cell after it was cooled to 30 °C before the baseline spectrum was recorded.

In-situ FTIR:

Self-supporting wafers (10-20 mg/cm²) were pressed and sealed in a heatable IR cell. The sample was reduced with H₂ at 200 °C for 0.5 h and cooled to 30 °C under dynamic vacuum. At this point, a baseline spectrum was recorded. Subsequent heating to 160 °C was performed at 10 °C/min, with a subsequent hold time of 10 min prior to acquisition of another base line spectrum. After the cell cooled to 30 °C, water was introduced into the cell by flowing CO through a water bubbler. The cell was heated to 160 °C to trigger the reaction and a series of representative FTIR spectra was recorded every 5 min.

GCMS:

Gas chromatograph-mass spectrometer (GC-MS) was measured on Agilent 7890-5975C instrument under the EI ionization model.

3. Catalytic Reactions

The catalytic reactions were carried out in a Teflon-lined stainless-steel autoclave. In a typical procedure, 50 mg catalyst, 3 ml 1,4-dioxane, 1 mmol n-Dodecane as the internal standard and 150 ul water were loaded into the reactor. The reactor was sealed and purged with Ar for three times. Then ethylene and CO were charged into the reactor to a certain pressure. The reactor was placed in a temperature-controlled steel stainless band heater. After quenching the reactor in an ice bath, products were collected and analyzed by gas chromatography (GC) with an HP-5 column.

Produced 3-pentanone is given as $\text{mmol}_{3\text{-pentanone}}/\text{mmol}_{\text{Rh}}$.

Selectivity is reported relative to all the products detected and given as $100 \% \cdot (\text{m}_{\text{propanal}} \text{ or } 2 \cdot \text{m}_{3\text{-pentanone}}) / (2 \cdot \text{m}_{3\text{-pentanone}} + \text{m}_{\text{propanal}})$.

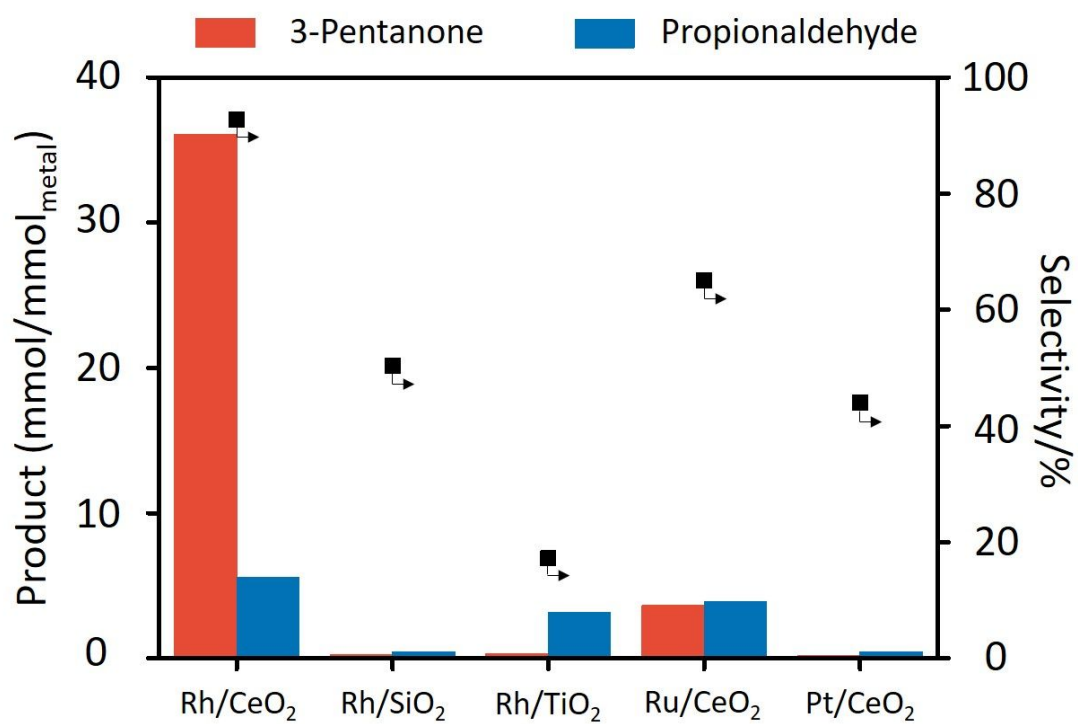


Figure S1. Ethylene carbonylation on various catalysts. Reaction conditions: 50 mg catalyst, 3 mmol ethylene, 1.0 MPa CO, 3 ml 1,4-dioxane, 150 μ l water, 1 mmol n-Dodecane as the internal standard, 160 $^{\circ}$ C, 4 h.

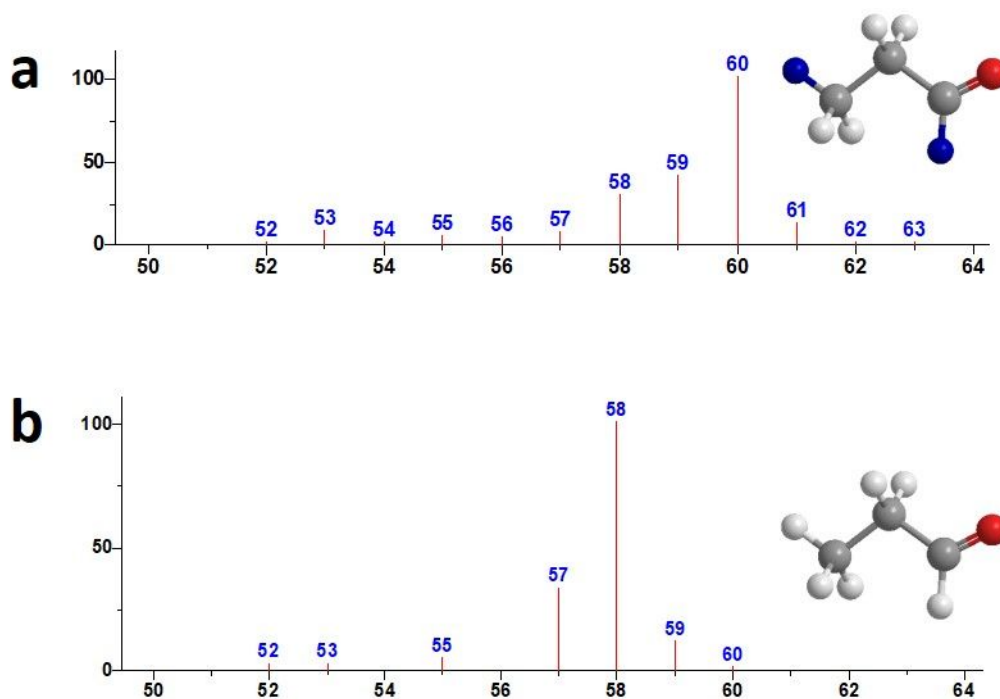


Figure S2. Mass spectra of propionaldehyde produced from ethylene carbonylation with (a) D₂O and (b) H₂O, red:O, grey:C, white:H, blue:D. (Reaction conditions: 50 mg Rh/CeO₂, 3 mmol ethylene, 1.0 MPa CO, 3 ml 1,4-dioxane, 150 ul water, 1 mmol n-Dodecane as the internal standard, 160 °C, 4 h)

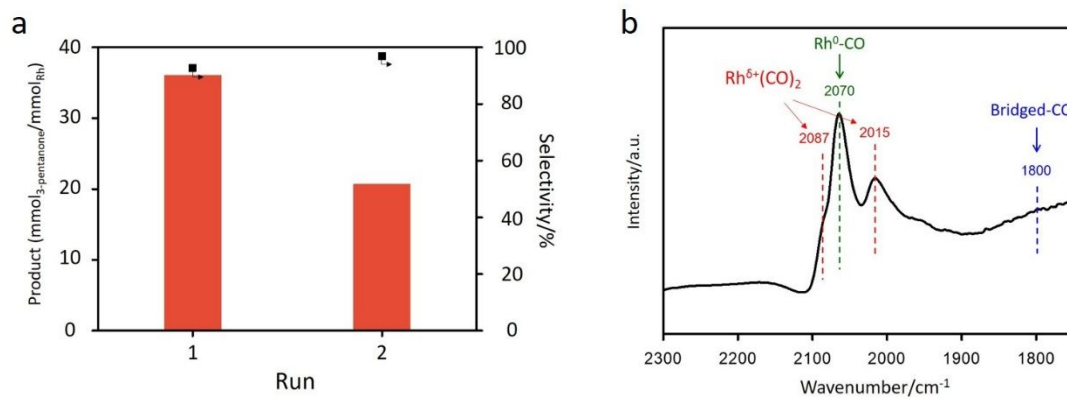


Figure S3. (a) Results of the recycling tests for ethylene carbonylation to 3-pentanone on Rh/CeO₂, (b) IR spectrum of CO adsorbed on the reused Rh/CeO₂.

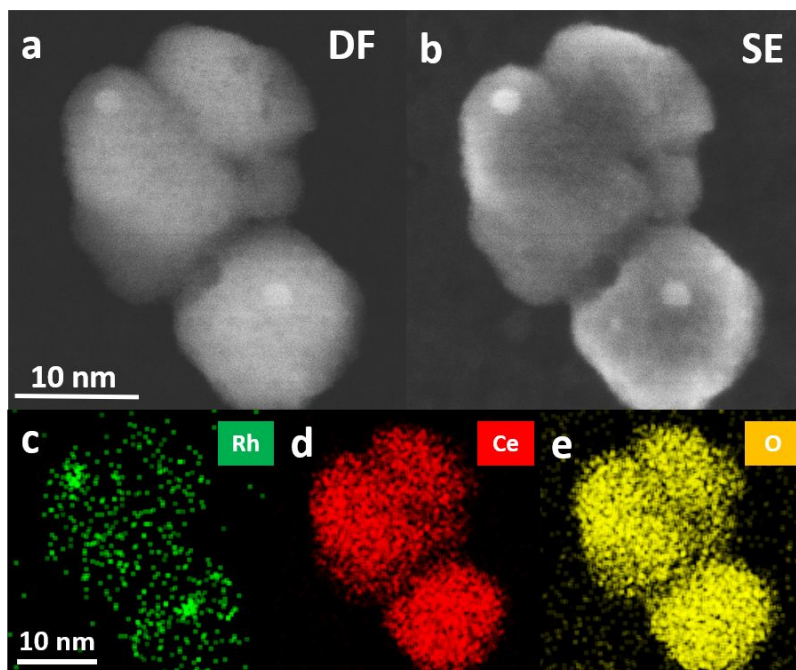


Figure S4. Dark field (DF) and secondary electron (SE) STEM images (a, b) and the corresponding EDX elemental mapping of Rh (c), Ce (d) and O (e) of Rh/CeO₂ catalyst.

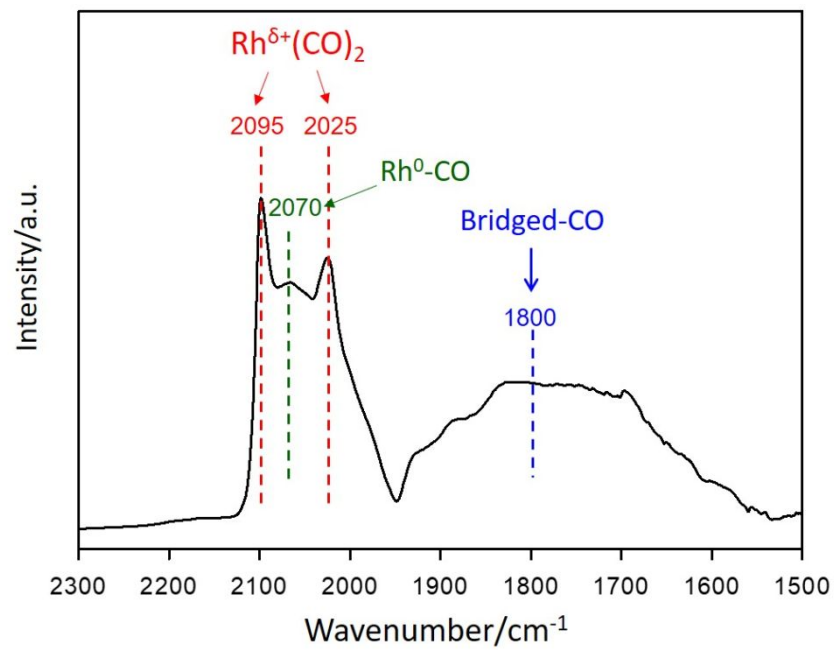


Figure S5. IR spectrum of CO adsorbed on Rh/CeO₂

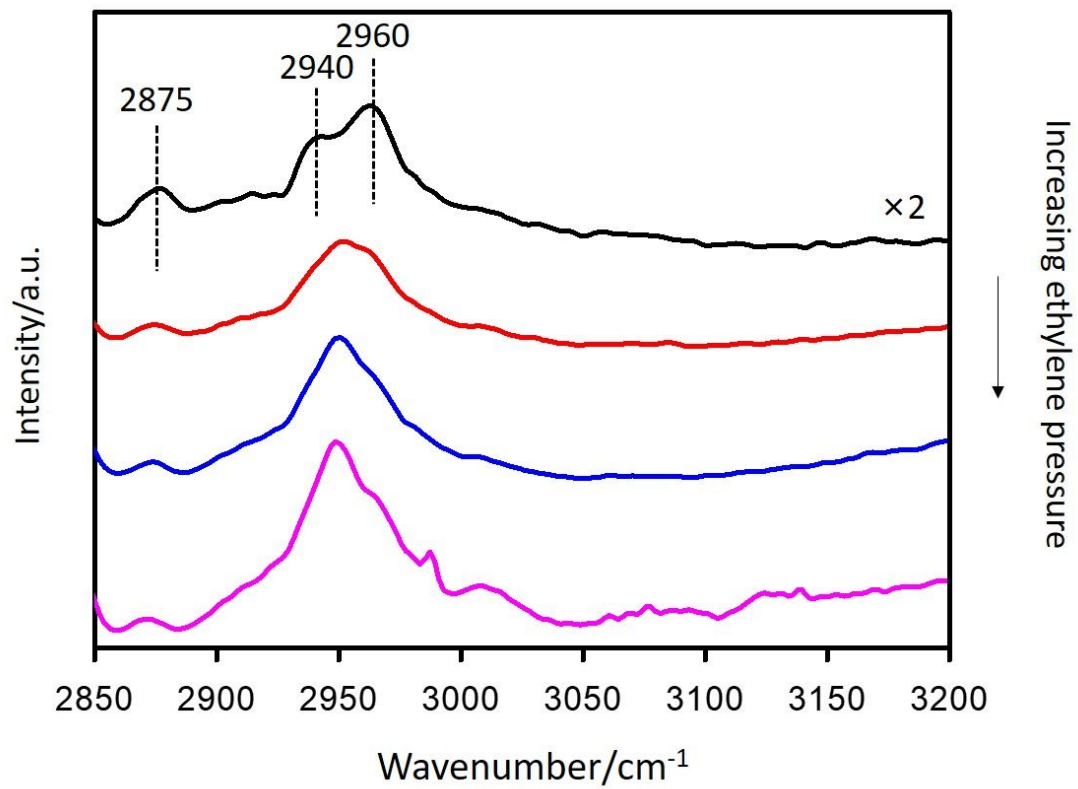


Figure S6. IR spectra of ethylene adsorbed on Rh/CeO₂ in the presence of water.

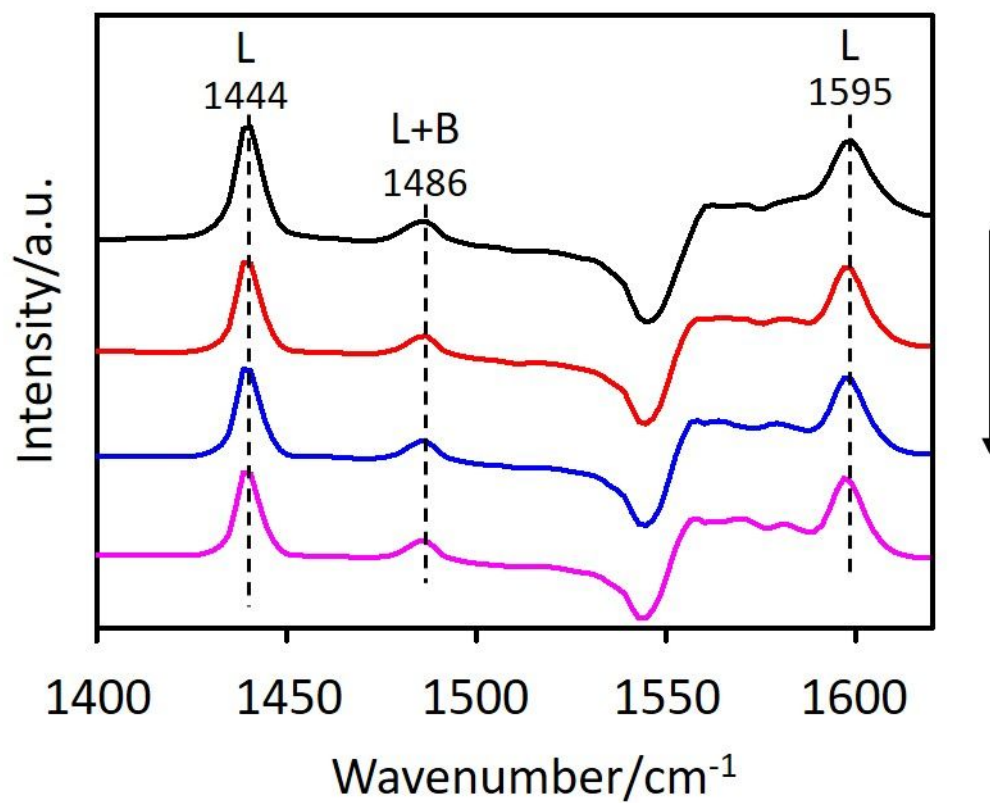
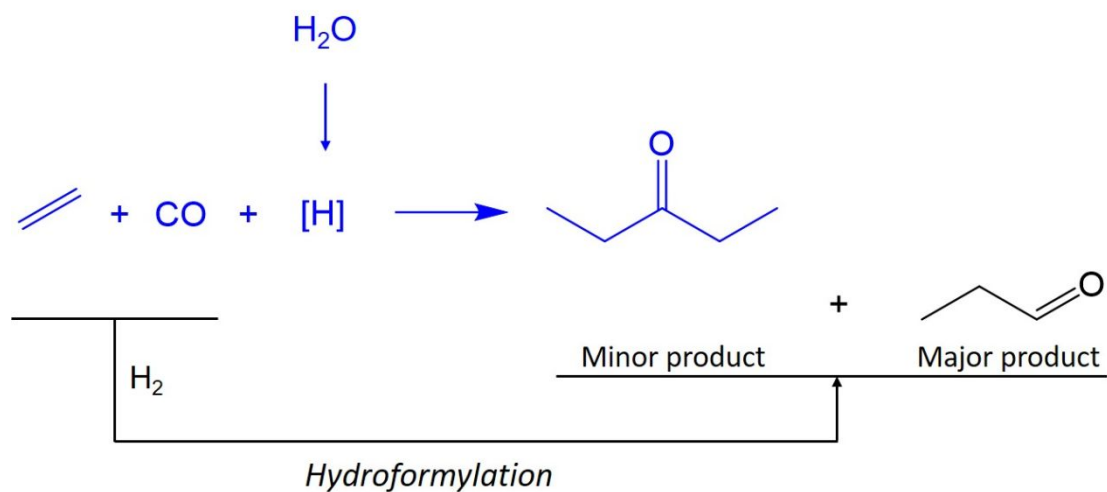
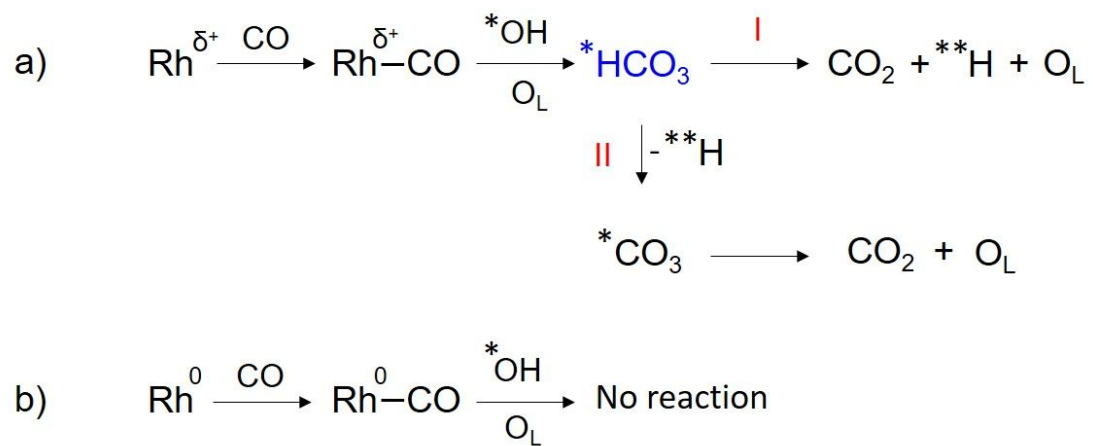


Figure S7. FTIR spectra after pyridine adsorption and evacuation in vacuo on CeO₂ after water pre-adsorption (The arrow indicates desorbing sequence of pyridine in vacuo).



Scheme S1. Schematic ethylene carbonylation to 3-pentanone with in-situ generated H via water gas shift reaction and ethylene hydroformylation with gaseous H_2 .



Scheme S2. Proposed water-gas-shift reaction mechanism on Rh/CeO₂ (O_L: Lattice oxygen of ceria;*: Oxygen vacancies of ceria;** :Rh surface).