Supporting Information

Hydride Species Induced Enhancement of CO₂ Hydrogenation

Selectivity on Ru Atom-modified CeO₂ Catalyst

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Synthesis of CeO₂-rod

The preparation of CeO₂-rod carrier was obtained by the common hydrothermal synthesis method. A certain amount (1.736 g) of cerium nitrate precursor was dissolved in 10 ml of deionized water and poured into the obtained NaOH solution at a concentration of 6.86 mol/L, after which the mixed solution was stirred for 1h and loaded into a polytetrafluoroethylene hydrothermal autoclave with 100ml for a hydrothermal treatment at 100°C for 24 h. Finally, the white precipitate was removed and washed several times with deionized water and ethanol until the pH of the solution was neutral, and the CeO₂-rod sample was obtained after drying and roasting at 600 °C.

Characterization of catalysts

Temperature-programmed surface experiments (TPSR) for CO₂ hydrogenation were performed on a Micromeritics AutoChem II 2920 with an on-line mass spectrometer (MS). The sample was first reduced with 5vol.% H₂/Ar (40 mL/min) at 500 °C for 1 h and purged with He at the same temperature for 30 min before the temperature was lowered to 30 °C. Subsequently, 5vol.%CO₂/Ar (40 mL/min) system and kept for 1h to saturate the adsorption, 5vol.% H₂/Ar (40 mL/min) was introduced after scrubbing with He. The catalyst was then heated from 30 °C to 800 °C at a rate of 10°C/min and MS signals at m/z = 16 (CH₄), 18 (H₂O), 28 (CO), and 44 (CO₂) were recorded on-line by a mass spectrometer.

Temperature programmed desorption (CO-TPD) experiments were carried out on a Micromeritics AutoChem II 2920 with online mass spectrometer, where after 60 min of reduction at 500 °C and cooling to room temperature, the gas stream was switched to 1vol.%CO/Ar) and adsorption was continued for 30 min until saturation. The desorption signals of CO(m/z=28) in He flow were recorded from 30 °C to 800 °C at 10 °C/min.

AFS Analysis

Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages that utilizes the FEFF6 program to fit the EXAFS data. The energy calibration of the sample was conducted through a standard Ru foil, which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The $\chi(k)$ data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The *k*2-weighted $\chi(k)$ data were Fourier transformed after applying a Hanning window function ($\Delta k = 1.0$). For EXAFS modeling, the global amplitude EXAFS (*CN*, *R*, σ^2 and ΔE_0) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS of the Ru foil is fitted and the obtained amplitude reduction factor S_0^2 value (0.854) was set in the EXAFS analysis to determine the coordination

numbers (CNs) in the Ru-O, Ru-Ru scattering path in sample.



Fig. S1. HAADF-STEM and HRTEM image of \mbox{CeO}_2



Fig. S2. The corresponding extracted line profiles of dual atom in Ru2/CeO₂.



Fig. S3. Arrhenius analysis of Ru/CeO₂ catalysts.



Fig. S4. Fourier transform of the EXAFS signals and the fitting curves in K space for $Ru1/CeO_2(A)$ and $Ru2/CeO_2(B)$ catalysts.



Fig. S5. Ce XPS spectra of Ru/CeO₂ catalysts.



Fig. S6. Relationship between the ratio of Ce^{3+} and CO_2 adsorption capacity.



Fig. S7. Relationship between methane and formate with temperature of Ru1/CeO₂.



Fig. S8. Relationship between CO and carboxylate with temperature of Ru2/CeO₂.



Fig. S9. CO_2 -TPSR profiles of Ru/CeO₂ catalysts.



Fig. S10. CO-TPD profiles of Ru/CeO₂ catalysts.



Figure S11. Calculated structures and oxygen vacancy formation energies of $Ru1/CeO_2$ and $Ru2/CeO_2$ catalysts.



Fig. S12. Calculated spin charge density difference (gray) and adsorption energies of CO_2 on the (A) Ru₁-CeO₂(110), (B) Ru₂-CeO₂(110) surfaces with oxygen vacancy. Left: top view, right: side view. The iso-surfaces are plotted at a value of 0.05 e/Å³. The dot lines of blue represent O vacancies. Red: O atoms; white: Ce atoms; navy blue: Ru atoms, black: C atoms; yellow: O atoms of CO_2 , this notation is used throughout the paper.



Figure S13. Calculated structure and adsorption energy of H_2 on the Ru1/CeO₂ surface.



Fig.S14. Calculated key structures and spin charge density differences of CO_2 hydrogenation on the Ru₁-CeO₂(110) surface. (A) initial state of CO_2 co-adsorption with 2H; (B) transition state and (C) final state of H⁺ attacking the O^{δ -} of CO₂ to form COOH; (D) transition state and (E) final state of H⁻ reacting with the C^{δ +} of CO₂ to produce HCOO.



Fig.S15. Calculated key structures and spin charge density differences of CO_2 hydrogenation on the Ru₂-CeO₂(110) surface. (A) initial state of CO₂ co-adsorption with 2H; (B) transition state and (C) final state of H attacking the O^{δ -} of CO₂ to form COOH; (D) transition state and \notin final state of H attacking the C^{δ +} of CO₂ to produce HCOO.

Sample	Shell	CNa	$R(\text{\AA})^b$	$\sigma^2({ m \AA}^2)^c$	$\Delta E_0(\mathrm{eV})^d$	R factor
Ru foil	Ru-Ru	12*	2.675 ± 0.002	0.0041±0.0003	-4.7±0.8	0.0053
RuO ₂	Ru-O	6.0±0.2	1.981 ± 0.006	$0.0032{\pm}\ 0.0004$	0.8±1.4	
	Ru-Ru	2.2±0.3	3.112±0.028	0.0053±0.0004	-6.6±6.5	0.0033
	Ru-Ru	7.9±0.5	3.568±0.019	0.0031±0.0002	0.8±1.8	
Ru1/CeO ₂	Ru-O	3.3±0.6	2.058±0.024	0.0056±0.0013	5.7±4.1	0.0051
Ru2/CeO ₂	Ru-O1	0.9±0.2	1.967±0.015	0 0108+0 0060	-1.3±3.2	0.0025
	Ru-O2	1.8±0.4	2.086±0.021	0.0100±0.0000		

TableS1. EXAFS fitting parameters at the Ru K-edge for various samples.

^{*a*}*CN*, coordination number; ^{*b*}*R*, the distance to the neighboring atom; ^{*c*} σ^2 , the Mean Square Relative Displacement (MSRD); ^{*d*} ΔE_0 , inner potential correction; *R* factor indicates the goodness of the fit. *S*0² was fixed to 0.854, according to the experimental EXAFS fit of Ru foil by fixing *CN* as the known crystallographic value. * This value was fixed during EXAFS fitting, based on the known structure of Ru. A reasonable range of EXAFS fitting parameters: 0.700 < *S*₀² < 1.000; *CN* > 0; σ^2 > 0 Å²; $|\Delta E_0| < 10$ eV; *R* factor < 0.02.

Table S2. H₂ desorption from H₂-TPD.

Samples	H ₂ uptake (umol/g)		
	50-200 °С	200-300 °С	
Ru1/CeO ₂	74	3.4	
Ru2/CeO ₂	134	/	