Theoretical Insights into Encapsulation-Induced CO_2 reduction Selectivity Reversal on Ru Supported on TiO_x Catalysts

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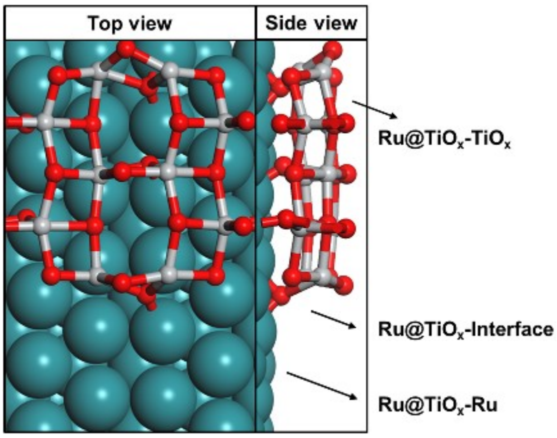

Figure S1. Optimized structure of Ru@TiO_2 catalyst. Ru: Green; Ti: Grey; O: Red.

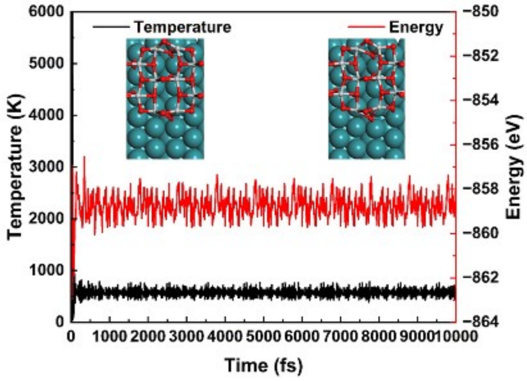

Figure S2. AIMD simulation result for Ru@TiO_x under 573K.

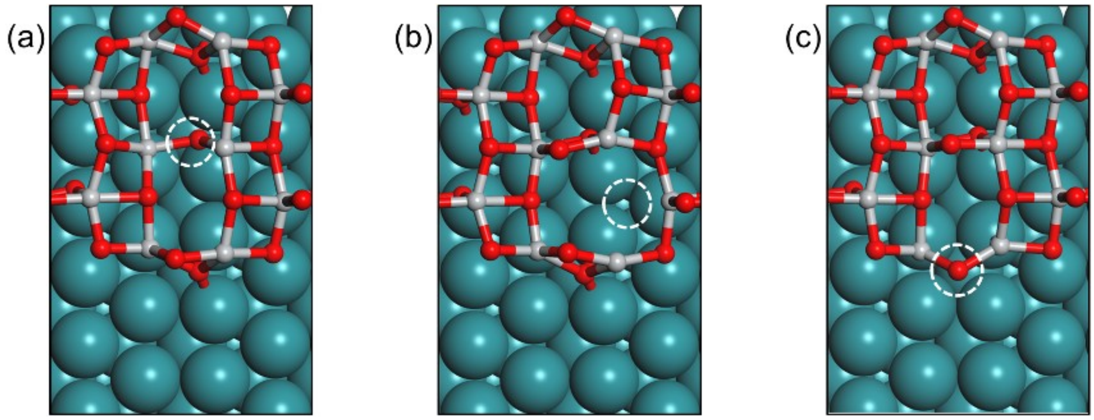

Figure S3. Optimized structures of (a) Ru@TiO_2-Ov_{2c}, (b) Ru@TiO_2-Ov_{3c}, and (c) the O_{2c} site located near the interface.

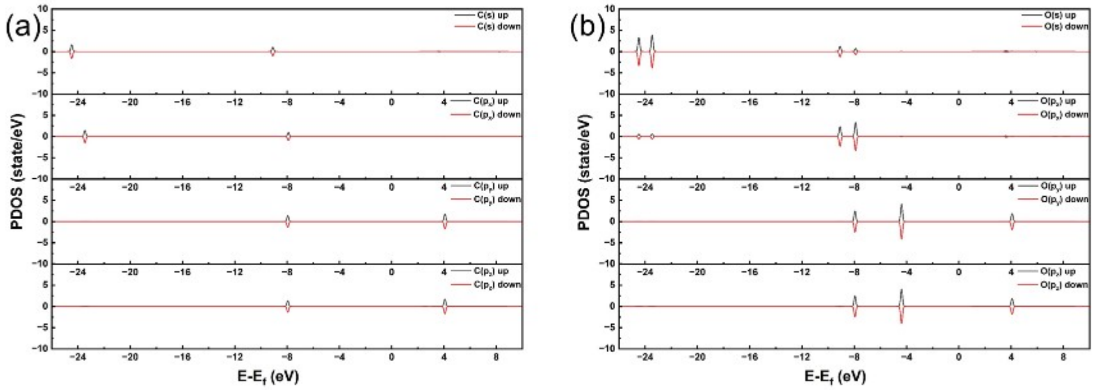

Figure S4. Projected density of states (PDOS) of the (a) C atom and (b) O atom in a free CO_2.

The following information can be obtained from the figure: (1) The p_x, p_y, and p_z orbitals of C, together with the s, p_x, p_y, and p_z orbitals of O, jointly contribute to the formation of the π orbital; (2) The p_y and p_z orbitals of O mainly form the lone pair orbital; (3) The p_y and p_z orbitals of C, along with the p_y and p_z orbitals of O, primarily contribute to the formation of the π* orbital. Therefore, the energy region dominated solely by the carbon p_x orbital corresponds to the π orbital.

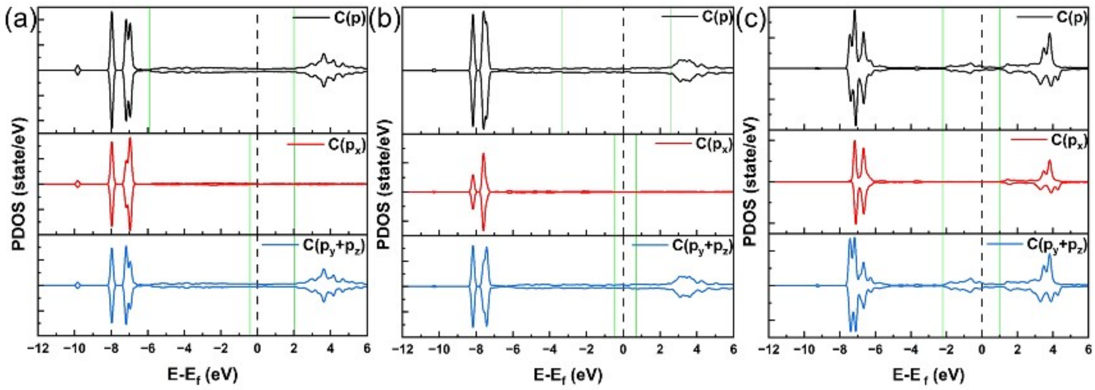

Figure S5. PDOS of C in CO_2 adsorbed on (a) Ru@TiO_x-Ru, (b) Ru@TiO_x-Interface, and (c) Ru@TiO_x-TiO_x.

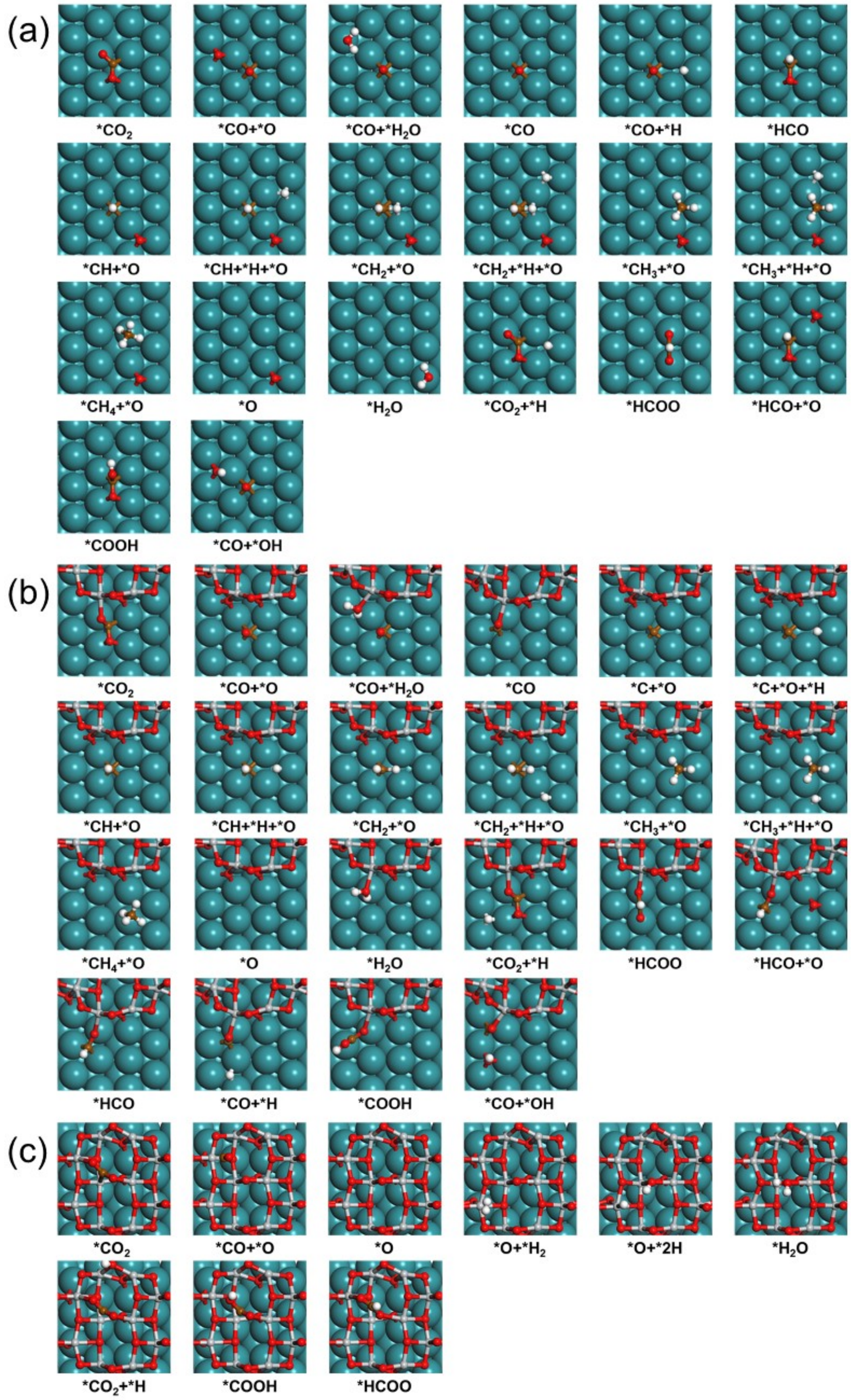

Figure S6. Optimized configurations of intermediates for CO_2 reduction on (a) Ru@TiO_x-Ru, (b) Ru@TiO_x-Interface, and (c) Ru@TiO_x-TiO_x. Ru: Green; Ti: Grey; O: Red; C:Brown; H:White.

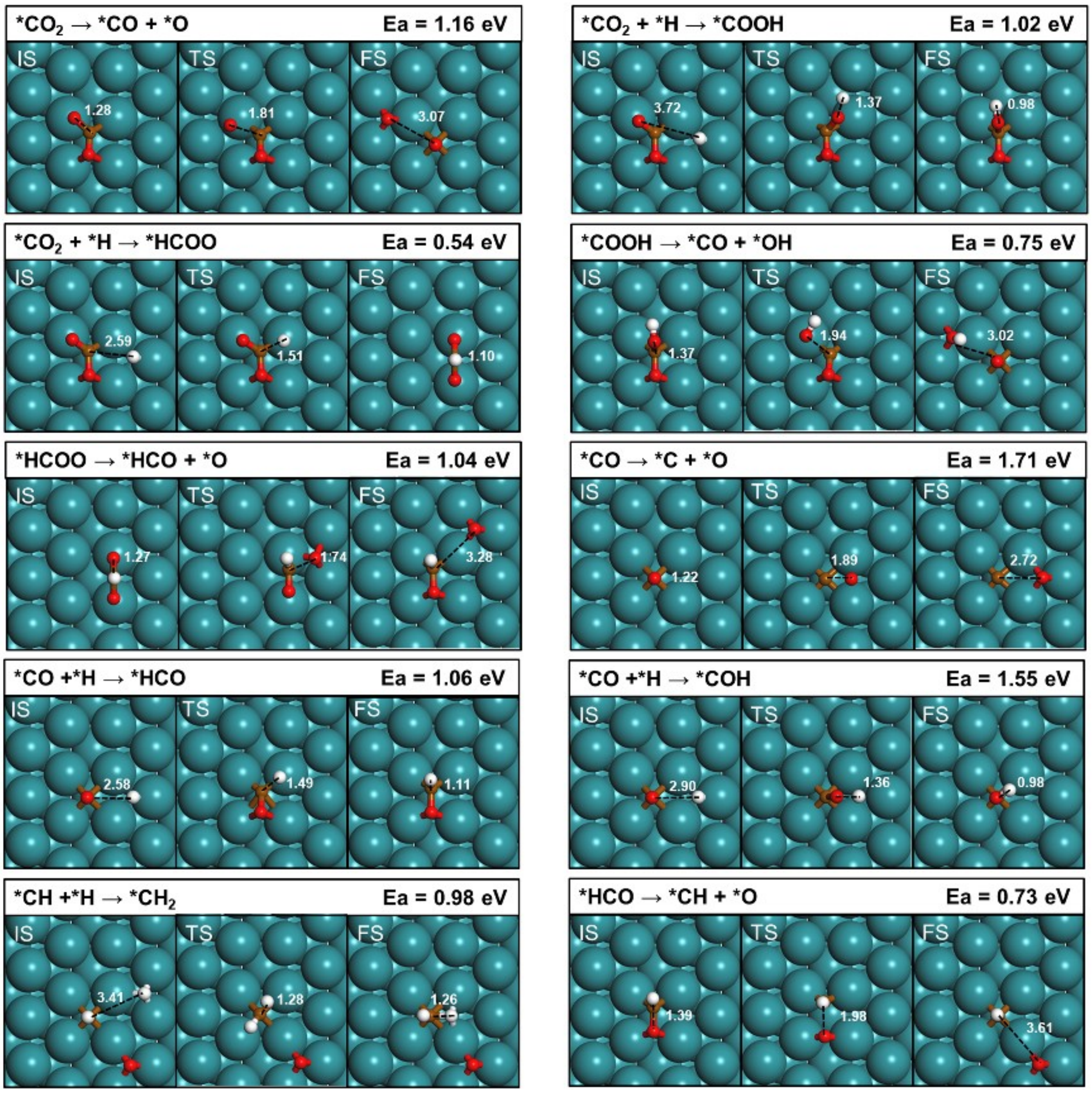

Figure S7. Structural evolution of key reaction steps on Ru@TiO_x-Ru, including initial state (IS), transition state (TS), and final state (FS). Ru: Green; Ti: Grey; O: Red; C: Brown; H: White. The distance unit is Å.

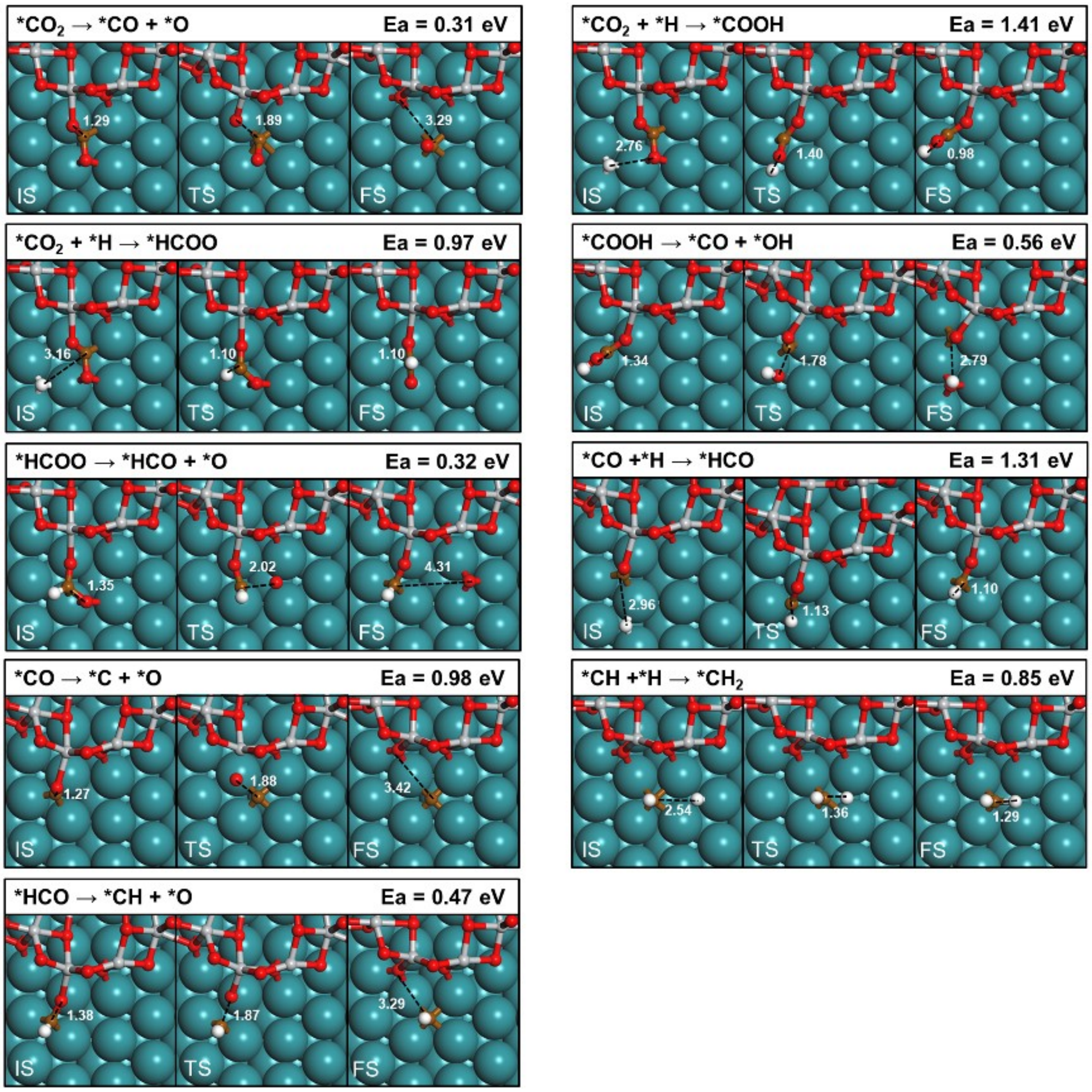

Figure S8. Structural evolution of key reaction steps on Ru@TiO_x-Interface, including initial state (IS), transition state (TS), and final state (FS). Ru: Green; Ti: Grey; O: Red; C: Brown; H: White. The distance unit is Å.

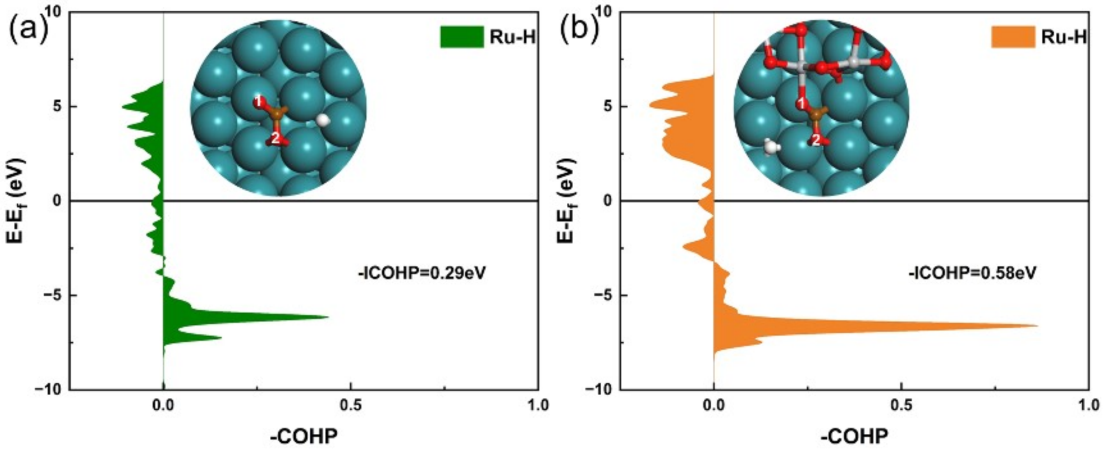

Figure S9. COHP analysis of Ru-H bond in (a) Ru@TiO_x-Ru and (b) Ru@TiO_x-Interface systems.

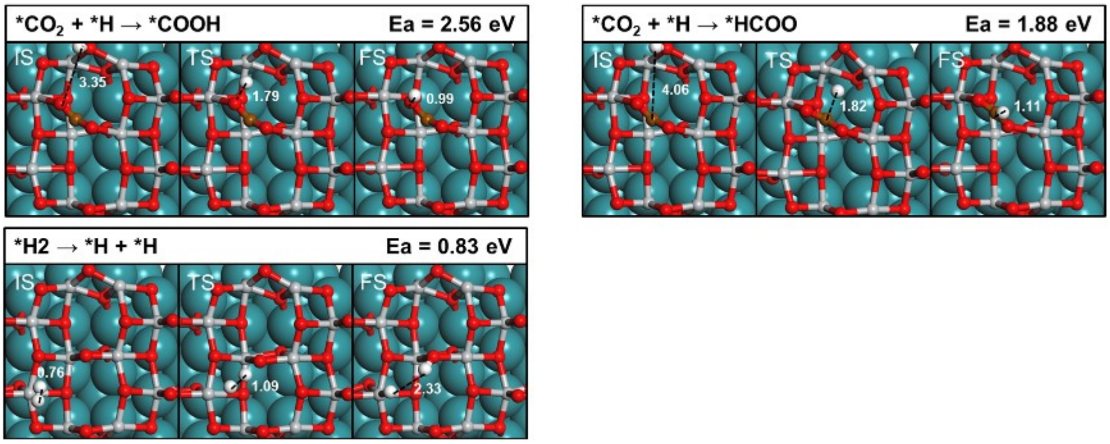

Figure S10. Structural evolution of key reaction steps on Ru@TiO_x-TiO_x, including initial state (IS), transition state (TS), and final state (FS). Ru: Green; Ti: Grey; O: Red; C: Brown; H: White. The distance unit is Å.

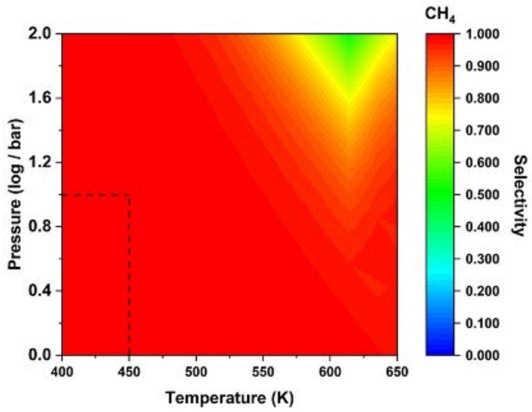

Figure S11. CH_4 selectivity on Ru@TiO_x-Interface as a function of pressure (1–20 bar) and temperature (400–650 K).

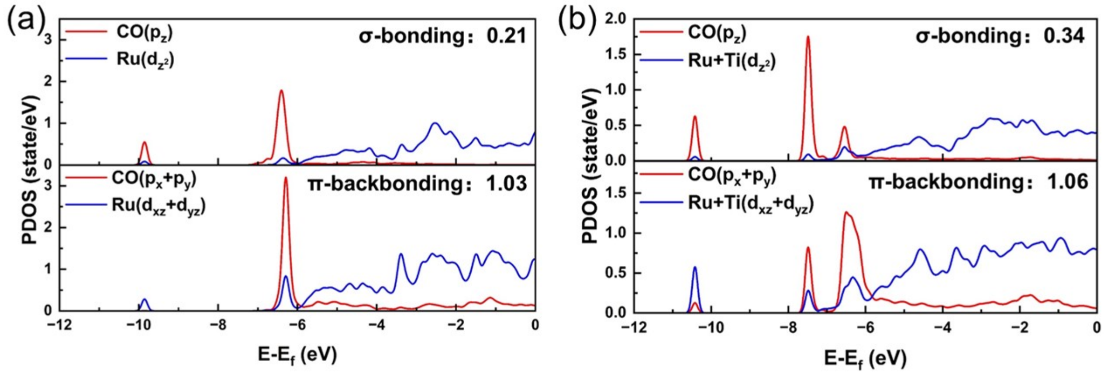

Figure S12. PDOS of CO_2 and Ru/Ti in (a) Ru@TiO_x-Ru and (b) Ru@TiO_x-Interface systems. The occupancies of σ-bonding and π-backbonding are presented at the upper right corner of each figure, which are obtained by integrating the overlapping peaks of the corresponding PDOS below the Fermi level.

Table S1. Formation Energies of Surface Oxygen Vacancies on TiO_2 in Different Catalysts.

	E_f /eV
p-TiO_2-Ov_{2c}	4.84
p-TiO_2-Ov_{3c}	5.33
Ru@TiO_x-Ov_{2c}	3.02
Ru@TiO_x-Ov_{3c}	4.88

Table S2. Structural parameters for CO_2 adsorption on perfect TiO_2 and oxygen-deficient TiO_x-Ov_{2c} surfaces.

Systems	E_{ads}(eV)	$d_{C\text{-}O1}$(Å)	$d_{C\text{-}O2}$(Å)	∠O-C-O(°)	Q_{CO2}(e)	Q_C in CO_2(e)	Q_{O1}/Q_{O2} in CO_2(e)
TiO_2	-0.23	1.33	1.21	130.43	-0.02	+0.16	-0.05/-0.13
TiO_x-Ov_{2c}	-0.40	1.24	1.27	135.11	-0.85	-0.69	-0.05/-0.11

Positive and negative values indicate electron loss and gain by CO_2 upon adsorption, respectively.

Table S3. Free energy changes (ΔG) for each step of CO_2 reduction reaction on Ru@TiO_x-Ru. * denotes the adsorption site, and all energy values are in eV.

Reaction steps	Ru@TiO_x-Ru
* + CO_2(g) +4H_2(g) ↔ *CO_2 + 4H_2(g)	-0.17
*CO_2 + 4H_2(g) ↔ *CO + *O+ 4H_2(g)	-1.14
*CO + *O+ 4H_2(g) ↔ *CO + *H_2O + 3H_2(g)	0.27
*CO + *H_2O + 3H_2(g) ↔ *CO + H_2O(g) + 3H_2(g)	0.16
*CO + H_2O(g) + 3H_2(g) ↔ *CO + *H + H_2O(g) + 5/2H_2(g)	-0.32
*CO + *H + H_2O(g) + 5/2H_2(g) ↔ *HCO + H_2O(g) + 5/2H_2(g)	0.77
*HCO+ H_2O(g) + 5/2H_2(g) ↔ *CH+*O+ H_2O(g) + 5/2H_2(g)	-1.20
*CH+*O+ H_2O(g) + 5/2H_2(g) ↔ *CH+*H + *O+ H_2O(g) + 2H_2(g)	-0.42
*CH+*H + *O+ H_2O(g) + 2H_2(g) ↔ *CH_2 + *O+ H_2O(g) + 2H_2(g)	0.94
*CH_2 + *O+ H_2O(g) + 2H_2(g) ↔ *CH_2+*H + *O+ H_2O(g) + 3/2H_2(g)	-0.30
*CH_2+*H + *O+ H_2O(g) + 3/2H_2(g) ↔ *CH_3 + *O+ H_2O(g) + 3/2H_2(g)	0.43
*CH_3 + *O+ H_2O(g) + 3/2H_2(g) ↔ *CH_3+*H + *O+ H_2O(g) + H_2(g)	-0.28
*CH_3+*H + *O+ H_2O(g) + H_2(g) ↔ *CH_4 + *O+ H_2O(g) + H_2(g)	0.07
*CH_4 + *O+ H_2O(g) + H_2(g) ↔ * + CH_4(g) + *O+ H_2O(g) + H_2(g)	-0.10
*O+H_2(g) + H_2O(g) + CH_4(g) ↔ *H_2O + H_2O(g) + CH_4(g)	0.63
*H_2O + H_2O(g) + CH_4(g) ↔ * + 2H_2O(g) + CH_4(g)	-0.13
Formate Pathway:	
*CO_2 + 4H_2(g) ↔ *CO_2 + *H + 7/2H_2(g)	-0.34
*CO_2 + *H + 7/2H_2(g) ↔*HCOO + 7/2H_2(g)	0.02
*HCOO + 7/2H_2(g) ↔ *HCO + *O + 7/2H_2(g)	-0.47
*HCO + *O + 7/2H_2(g) ↔ *HCO + H_2O(g) + 5/2H_2(g)	0.52
Carboxyl Pathway:	
*CO_2 + *H + 7/2H_2(g) ↔ *COOH + 7/2H_2(g)	0.33
*COOH + 7/2H_2(g) ↔ *CO + *OH + 7/2H_2(g)	-1.00
*CO + *OH + 7/2H_2(g) ↔ *CO + H2O(g) + 3H_2(g)	0.29
The other competing pathways:	
*CO + H_2O(g) + 3H_2(g) ↔ * + CO(g) + H_2O(g) + 3H_2(g)	1.55
*CO + H_2O(g) + 3H_2(g) ↔ *C + *O + H_2O(g) + 3H_2(g)	0.06
*CO + *H + H_2O(g) + 5/2H_2(g) ↔ *COH + H_2O(g) + 5/2H_2(g)	0.63
*HCO+*H + H_2O(g) + 2H_2(g) ↔ *H_2CO + H_2O(g) + 2H_2(g)	0.43
*HCO+*H + H_2O(g) + 2H_2(g) ↔ *HCOH + H_2O(g) + 2H_2(g)	1.06

Table S4. Free energy changes (ΔG) for each step of CO_2 reduction reaction on Ru@TiOx-Interface. * denotes the adsorption site, and all energy values are in eV.

Reaction steps	Ru@TiO_x-Interface
Direct Dissociation Pathway:	
* + CO_2(g) +4H_2(g) ↔ *CO_2 + 4H_2(g)	-0.42
*CO_2 + 4H_2(g) ↔ *CO + *O+ 4H_2(g)	-1.44
*CO + *O+ 4H_2(g) ↔ *CO + *H_2O + 3H_2(g)	0.78
*CO + *H_2O + 3H_2(g) ↔ *CO + H_2O(g) + 3H_2(g)	-0.22
*CO + H_2O(g) + 3H_2(g) ↔ *C + *O + H_2O(g) + 3H_2(g)	-0.30
*C + *O + H_2O(g) + 3H_2(g) ↔ *C + *O + *H + H_2O(g) + 5/2H_2(g)	-0.22
*C + *O + *H + H_2O(g) + 5/2H_2(g) ↔ *CH + *O + H_2O(g) + 5/2H_2(g)	-0.29
*CH + *O+ H_2O(g) + 5/2H_2(g) ↔ *CH + *H + *O+ H_2O(g) + 2H_2(g)	-0.23
*CH + *H + *O+ H_2O(g) + 2H_2(g) ↔ *CH_2 + *O+ H_2O(g) + 2H_2(g)	0.87
*CH_2 + *O+ H_2O(g) + 2H_2(g) ↔ *CH_2+*H + *O+ H_2O(g) + 3/2H_2(g)	-0.22
*CH_2+*H + *O+ H_2O(g) + 3/2H_2(g) ↔ *CH_3 + *O+ H_2O(g) + 3/2H_2(g)	0.35
*CH_3 + *O+ H_2O(g) + 3/2H_2(g) ↔ *CH_3 + *H + *O+ H_2O(g) + H_2(g)	0.06
*CH_3+*H + *O+ H_2O(g) + H_2(g) ↔ *CH_4 + *O+ H_2O(g) + H_2(g)	-0.24
*CH_4 + *O+ H_2O(g) + H_2(g) ↔ * + CH_4(g) + *O+ H_2O(g) + H_2(g)	-0.02
*O + H_2(g) + H_2O(g) + CH_4(g) ↔ *H_2O + H_2O(g) + CH_4(g)	0.62
*H_2O + H_2O(g) + CH_4(g) ↔ * + 2H_2O(g) + CH_4(g)	0.29
Formate Pathway:	
*CO_2 + 4H_2(g) ↔ *CO_2 + *H + 7/2H_2(g)	-0.49
*CO_2 + *H + 7/2H_2(g) ↔*HCOO + 7/2H_2(g)	0.46
*HCOO + 7/2H_2(g) ↔ *HCO + *O + 7/2H_2(g)	-0.67
*HCO + *O + 7/2H_2(g) ↔ *HCO + H_2O(g) + 5/2H_2(g)	0.52
*HCO+ H_2O(g) + 5/2H_2(g) ↔ *CH+*O+ H_2O(g) + 5/2H_2(g)	-1.52
Carboxyl Pathway:	
*CO_2 + *H + 7/2H_2(g) ↔ *COOH + 7/2H_2(g)	0.65
*COOH + 7/2H_2(g) ↔ *CO + *OH + 7/2H_2(g)	-1.17
*CO + *OH + 7/2H_2(g) ↔ *CO + H2O(g) + 3H_2(g)	0.12
The other competing pathways:	
*CO + H_2O(g) + 3H_2(g) ↔ * + CO(g) + H_2O(g) + 3H_2(g)	1.98
*CO + *H + H_2O(g) + 5/2H_2(g) ↔ *COH + H_2O(g) + 5/2H_2(g)	1.21
*HCO+*H + H_2O(g) + 2H_2(g) ↔ *H_2CO + H_2O(g) + 2H_2(g)	0.29
*HCO+*H + H_2O(g) + 2H_2(g) ↔ *HCOH + H_2O(g) + 2H_2(g)	0.97

Table S5. Free energy changes (ΔG) for each step of CO_2 reduction reaction on Ru@TiO_x-TiO_x. * denotes the adsorption site, and all energy values are in eV.

Reaction steps	Ru@TiO_x-TiO_x
Direct Dissociation Pathway:	
* + CO_2(g) + H_2(g) ↔ *CO_2 + H_2(g)	0.29
*CO_2 + H_2(g) ↔ *CO + *O + H_2(g)	0.05
*CO + *O + H_2(g) ↔ *O + CO(g) + H_2(g)	-0.12
*O + CO(g) + H_2(g) ↔ *O + *H_2 + CO(g)	0.29
*O + *H_2 + CO(g) ↔ *O + *2H + CO(g)	0.67
*O + *2H + CO(g) ↔ *H_2O + CO(g)	-1.00
*H_2O + CO(g) ↔ CO(g)+ H_2O(g)	0.46
Formate Pathway:	
*CO_2 + *H +1/2H_2 ↔ *HCOO	-0.92
Carboxyl Pathway:	
*CO_2 + *H +1/2H_2 ↔ *COOH	0.79
The other competing pathways:	
*CO + *O + H_2(g) ↔ *C + *O + *O + H_2(g)	6.00
*CO + *H +1/2H_2(g) ↔ *HCO +1/2H_2(g)	0.99
*CO + *H +1/2H_2(g) ↔ *COH + 1/2H_2(g)	2.81

Table S6. Adsorption energies of oxygen-containing intermediates in the Ru@TiO_x-Ru and Ru@TiO_x-Interface systems, and all energy values are in eV.

adsorbates	Ru@TiO_x-Ru	Ru@TiO_x-Interface
O	-6.42	-6.83
CO_2	-0.78	-1.06
HCO	-3.42	-3.59
COH	-5.29	-5.33
H_2CO	-2.01	-2.27
HCOH	-4.53	-4.79
HCOO	-3.85	-3.86
COOH	-3.21	-3.33

Table S7. Definitions of the symbols used in the free-energy profiles of Ru@TiO_x-Ru, Ru@TiO_x-Interface, and Ru@TiO_x-TiO_x.

Ru@TiO_x-Ru:	
CO_2(g)	* + CO_2(g) +4H_2(g)
*CO_2	*CO_2 + 4H_2(g)
*CO + *O	*CO + *O+ 4H_2(g)
*CO + *H_2O	*CO + *H_2O + 3H_2(g)
*CO	*CO + H_2O(g) + 3H_2(g)
*CO + *H	*CO + *H + H_2O(g) + 5/2H_2(g)
*HCO	*HCO + H_2O(g) + 5/2H_2(g)
*CH+*O	*CH + *O+ H_2O(g) + 5/2H_2(g)
*CH+*H + *O	*CH + *H + *O + H_2O(g) + 2H_2(g)
*CH_2 + *O	*CH_2 + *O + H_2O(g) + 2H_2(g)
*CH_2+*H + *O	*CH_2+*H + *O+ H_2O(g) + 3/2H_2(g)
*CH_3 + *O	*CH_3 + *O+ H_2O(g) + 3/2H_2(g)
*CH_3+*H + *O	*CH_3+*H + *O+ H_2O(g) + H_2(g)
*CH_4 + *O	*CH_4 + *O+ H_2O(g) + H_2(g)
*O	*O + CH_4(g) + H_2O(g) + H_2(g)
*H_2O	*H_2O + H_2O(g) + CH_4(g)
*	* + 2H_2O(g) + CH_4(g)
*CO_2 + *H	*CO_2 + *H + 7/2H_2(g)
*HCOO	*HCOO + 7/2H_2(g)
*HCO + *O	*HCO + *O + 7/2H_2(g)
*HCO	*HCO + H_2O(g) + 5/2H_2(g)
*COOH	*COOH + 7/2H_2(g)
*CO + *OH	*CO + *OH + 7/2H_2(g)
CO(g)	* + CO(g) + H_2O(g) + 3H_2(g)
*C + *O	*C + *O + H_2O(g) + 3H_2(g)
*COH	*COH + H_2O(g) + 5/2H_2(g)
*H_2CO	*H_2CO + H_2O(g) + 2H_2(g)
*HCOH	*HCOH + H_2O(g) + 2H_2(g)
Ru@TiO_x-Interface:	
CO_2(g)	* + CO_2(g) +4H_2(g)
*CO_2	*CO_2 + 4H_2(g)
*CO + *O	*CO + *O + 4H_2(g)
*CO + *H_2O	*CO + *H_2O + 3H_2(g)
*CO	*CO + H_2O(g) + 3H_2(g)
*C + *O	*C + *O + H_2O(g) + 3H_2(g)
*C + *H + *O	*C + *O + *H + H_2O(g) + 5/2H_2(g)
*CH + *O	*CH + *O + H_2O(g) + 5/2H_2(g)
*CH + *H + *O	*CH + *H + *O+ H_2O(g) + 2H_2(g)

$*CH_2 + *O$	$*CH_2 + *O + H_2O(g) + 2H_2(g)$
$*CH_2+*H + *O$	$*CH_2+*H + *O+ H_2O(g) + 3/2H_2(g)$
$*CH_3 + *O$	$*CH_3 + *O+ H_2O(g) + 3/2H_2(g)$
$*CH_3+*H + *O$	$*CH_3+*H + *O+ H_2O(g) + H_2(g)$
$*CH_4 + *O$	$*CH_4 + *O + H_2O(g) + H_2(g)$
*O	$*O + CH_4(g) + H_2O(g) + H_2(g)$
$*H_2O$	$*H_2O + H_2O(g) + CH_4(g)$
*	$* + 2H_2O(g) + CH_4(g)$
$*CO_2 + *H$	$*CO_2 + *H + 7/2H_2(g)$
*HCOO	$*HCOO + 7/2H_2(g)$
*HCO + *O	$*HCO + *O + 7/2H_2(g)$
*HCO	$*HCO + H_2O(g) + 5/2H_2(g)$
*COOH	$*COOH + 7/2H_2(g)$
*CO + *OH	$*CO + *OH + 7/2H_2(g)$
CO(g)	$* + CO(g) + H_2O(g) + 3H_2(g)$
*COH	$*COH + H_2O(g) + 5/2H_2(g)$
$*H_2CO$	$*H_2CO + H_2O(g) + 2H_2(g)$
*HCOH	$*HCOH + H_2O(g) + 2H_2(g)$
Ru@TiO_x-TiO_x:	
$CO_2(g)$	$* + CO_2(g) + H_2(g)$
$*CO_2$	$*CO_2 + H_2(g)$
*CO + *O	$*CO + *O + H_2(g)$
*O	$*O + CO(g) + H_2(g)$
$*O + *H_2$	$*O + *H_2 + CO(g)$
*O + *2H	*O + *2H + CO(g)
$*H_2O$	$*H_2O + CO(g)$
*	$* + CO(g)+ H_2O(g)$
$*CO_2 + *H$	$*CO_2 + *H +1/2H_2$
*HCOO	$*HCOO + 1/2H_2$
*COOH	$*COOH + 1/2H_2$
*C + *O +*O	$*C + *O +*O + H_2(g)$
*HCO	$*HCO +1/2H_2(g)$
*COH	$*COH + 1/2H_2(g)$