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Supporting information

DFT-Based Microkinetic Model Analysis of Dry Reforming of Methane over $Ru_7/CeO_2(111)$ and $Ru_7/CeO_2(110)$: Key Role of Surface Lattice Oxygen Vacancy

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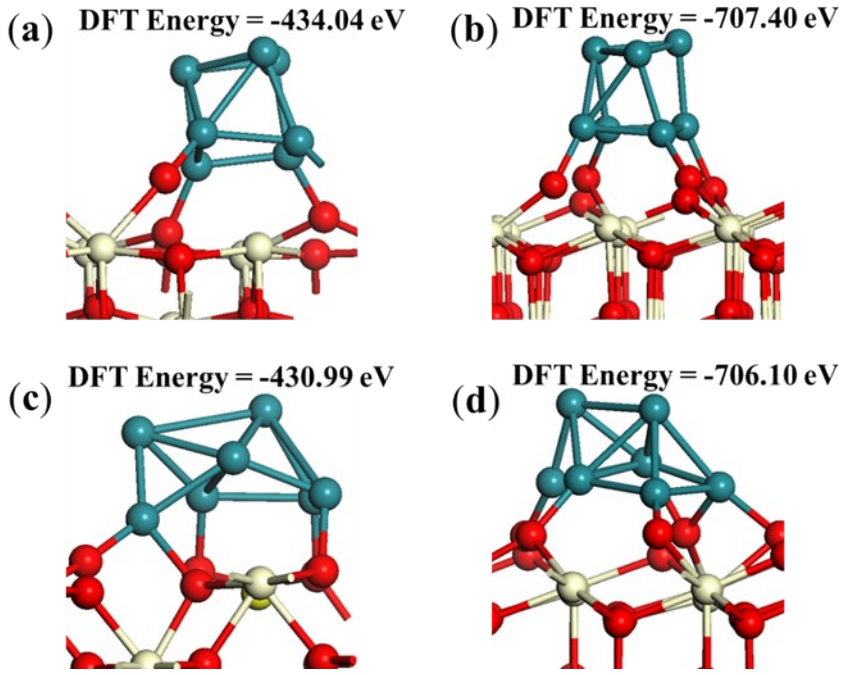


Fig. S1 (a) Stable configurations of Ru7 on CeO2(110), (b) stable configurations of Ru7 on CeO2(111), (c) metastable configurations of Ru7 on CeO2(110), (d) configurations of Ru7 on CeO2(111)

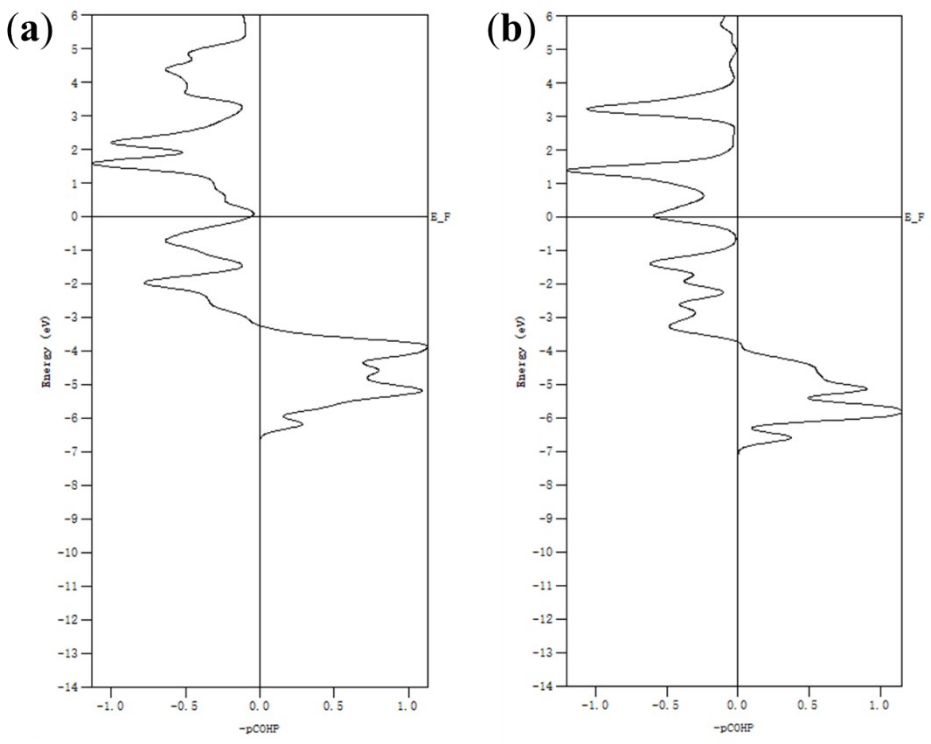


Fig. S2 Crystal orbital Hamilton population (COHP) analysis for the nearest-neighbor interactions between O-Ru bond in (a) $Ru_7/CeO_2(110)$ and (b) $Ru_7/CeO_2(111)$

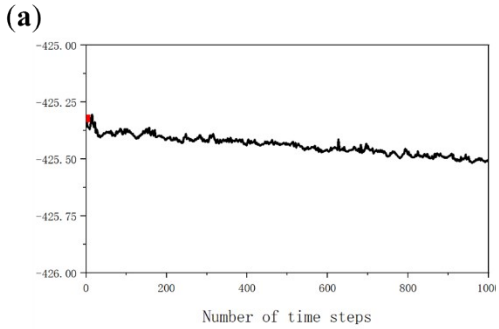


Fig. S3 (a)Energy evolution versus the MD simulation steps at 1200 K for Ru7/CeO2(110), (b) the changes of bond distance between Ru and Ru atom during MD simulation

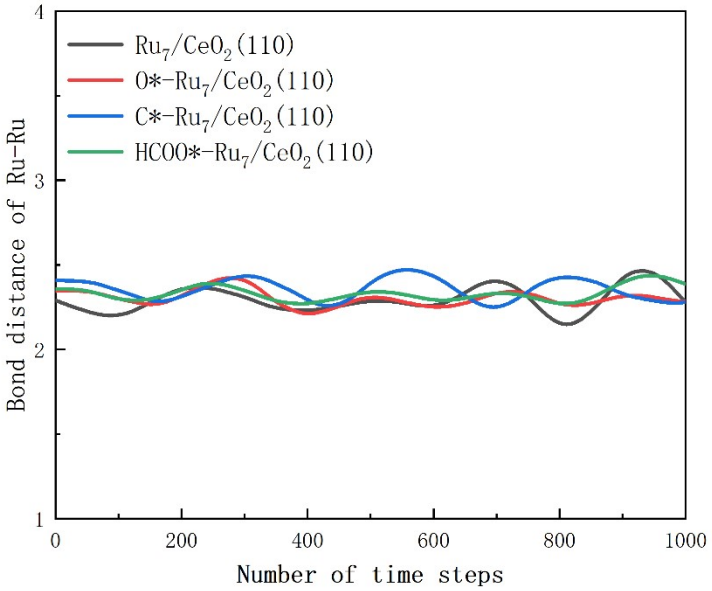
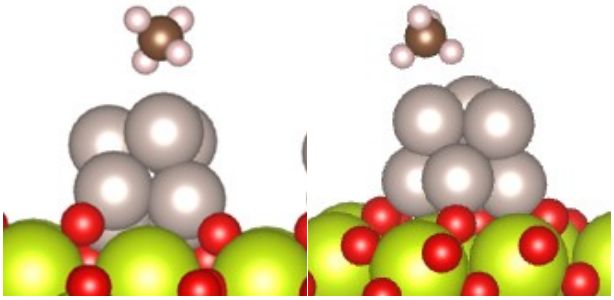
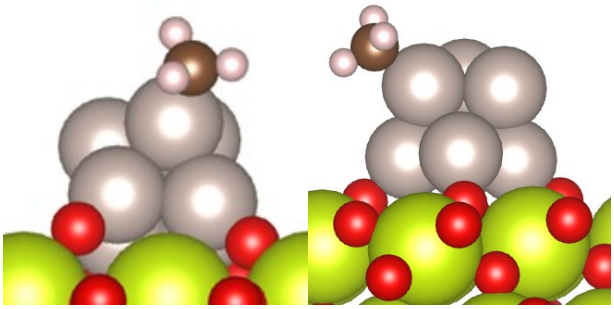


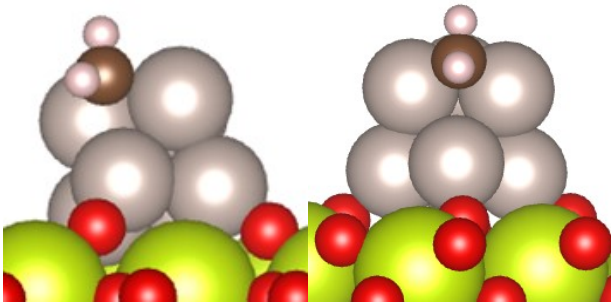
Fig. S4 The changes of bond distance between Ru and Ru atom during MD simulation for $Ru_7/CeO_2(110)$, the $Ru_7/CeO_2(110)$ adsorbed intermediate O*(O*-Ru_7/CeO_2), C*(C*-Ru_7/CeO_2) and HCOO*(HCOO*-Ru_7/CeO_2).



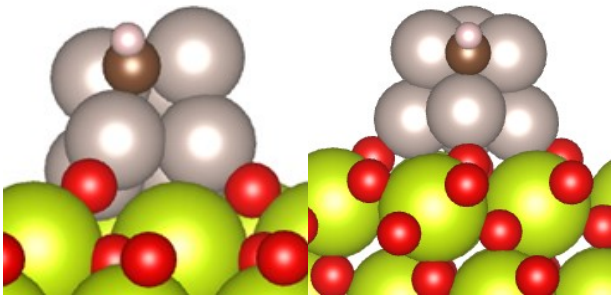
CH_4*



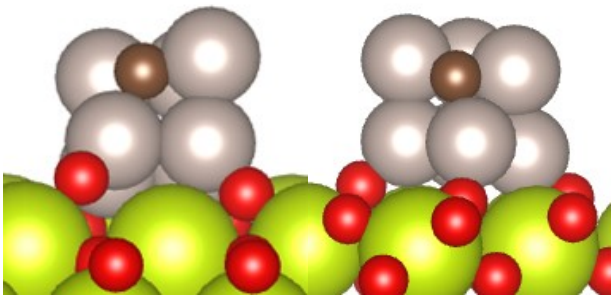
CH_3*



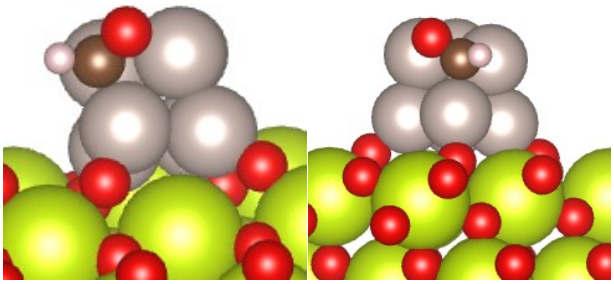
CH_2*



CH*



C*



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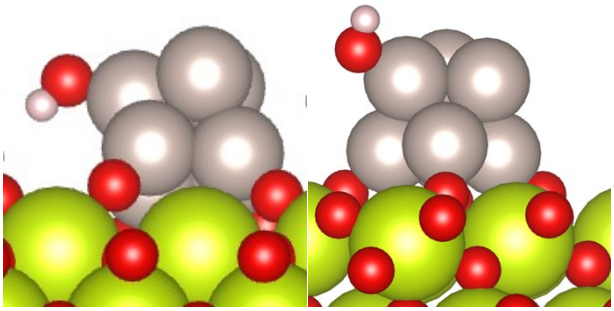
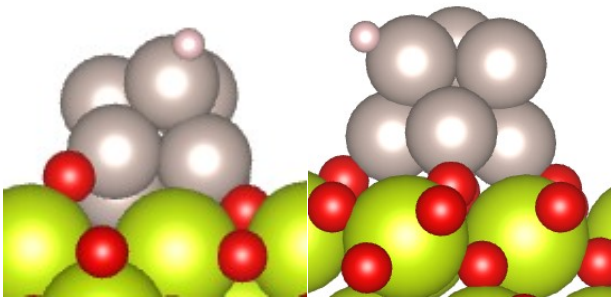
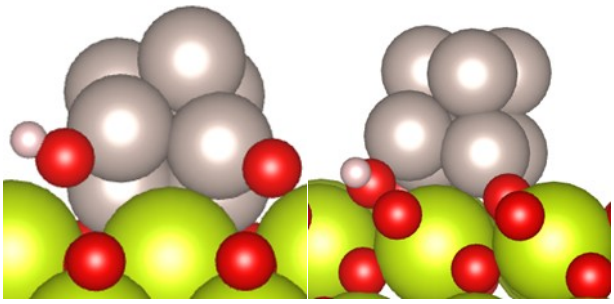


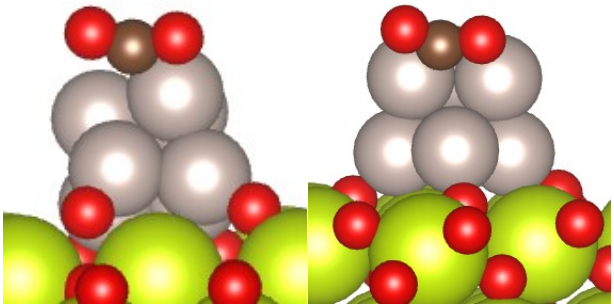
OH*



H*



H-O_L



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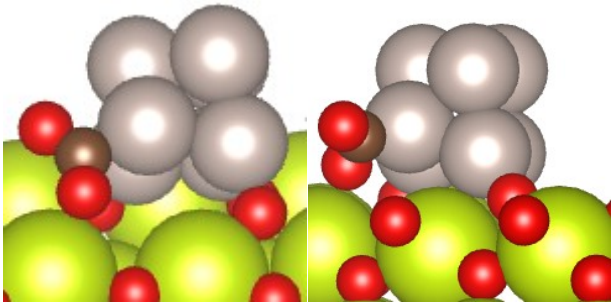
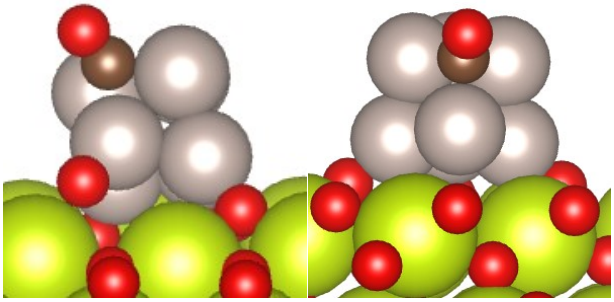
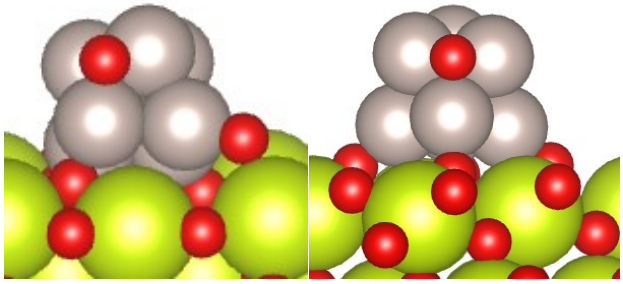


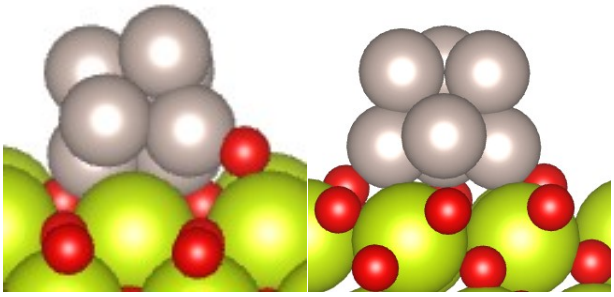
CO_2#



CO*



O*



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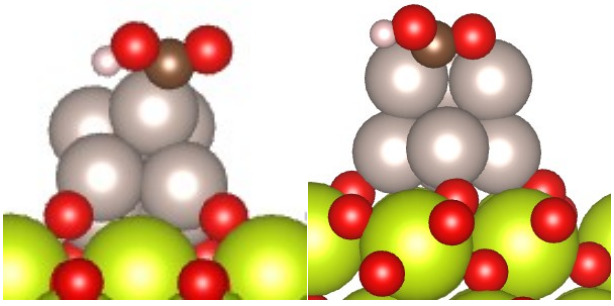


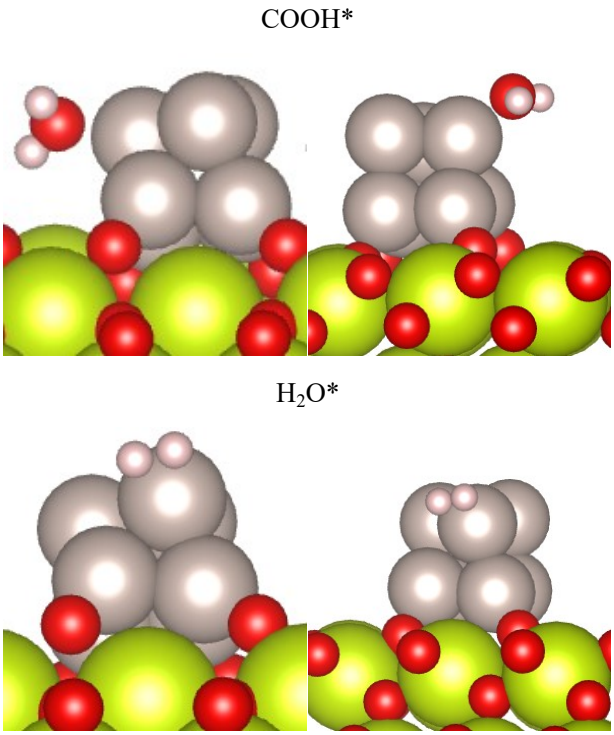


Fig. S5 Adsorption structure of key species on $Ru_7/CeO_2(110)$ and $Ru_7/CeO_2(111)$

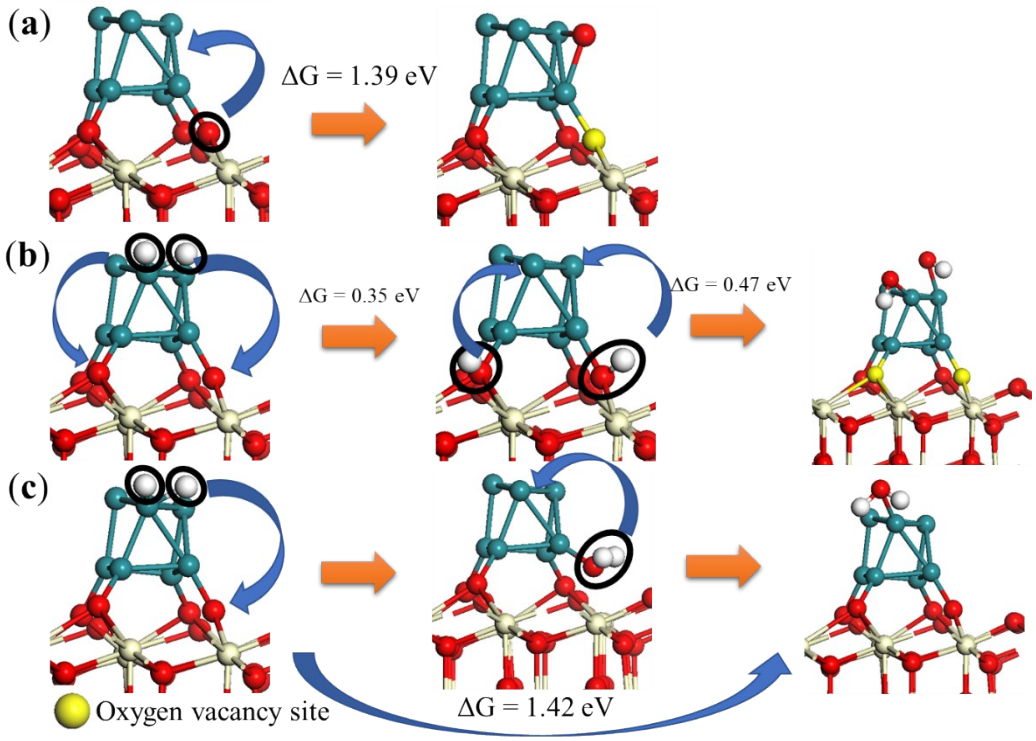


Fig. S6 The mechanism of formation oxygen vacancy site and standard free energy (Δ_rG^0) at 1000K for $Ru_7/CeO_2(111)$: (a) the oxygen reverse spillover mechanism, (b) the mechanism of H-assisted

oxygen reverse spillover mechanism, and (c) the mechanism of 2H with surface O# to form H_2O.

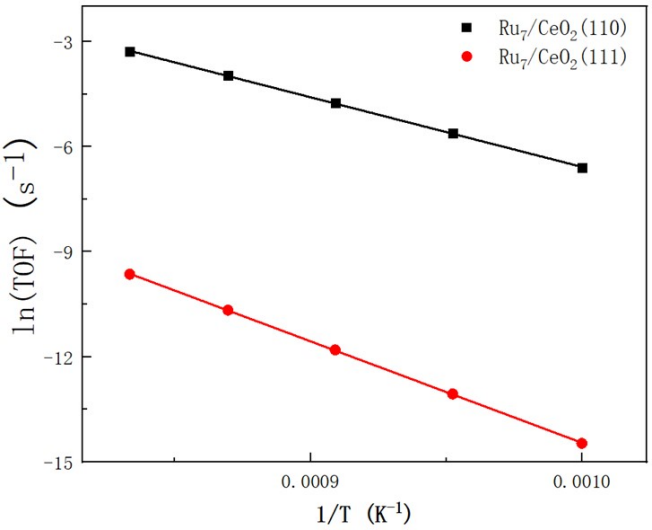


Fig. S7 The variation law of ln(TOF) with 1/T over $Ru_7/CeO_2(110)$ and $Ru_7/CeO_2(111)$

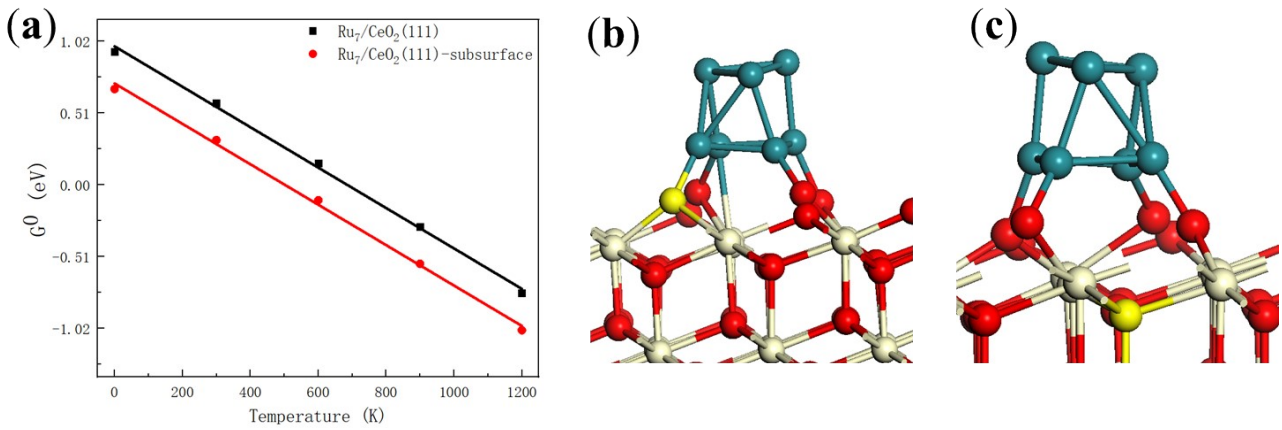
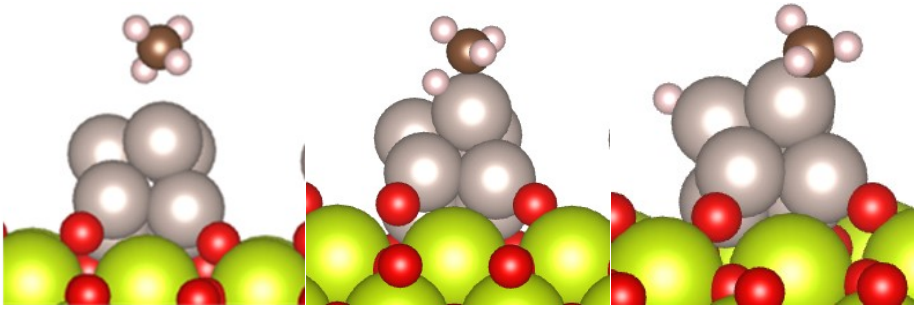
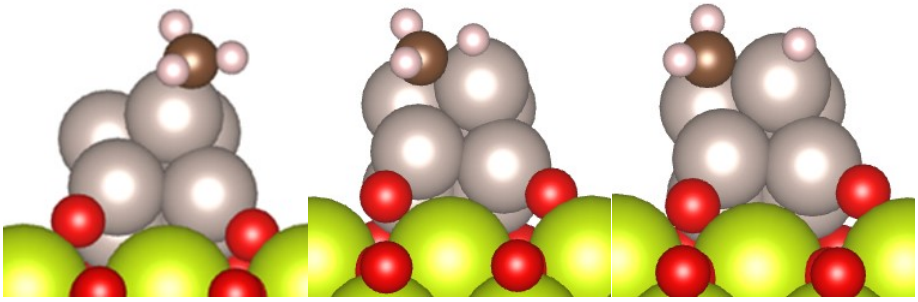


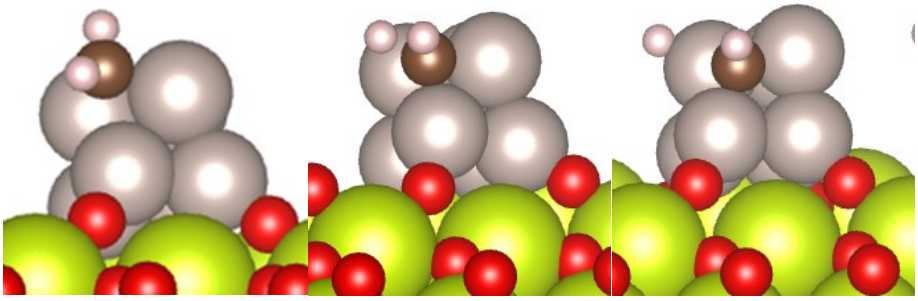
Fig. S8 (a) Plot of the variety for the formation of oxygen vacancy with temperature (black line: oxygen vacancy on surface for $Ru_7/CeO_{2-x}(111)$, red line: oxygen vacancy on subsurface for $Ru_7/CeO_{2-x}(111)$), (b) surface oxygen vacancy on $Ru_7/CeO_{2-x}(111)$, (c) subsurface oxygen vacancy on $Ru_7/CeO_{2-x}(111)$



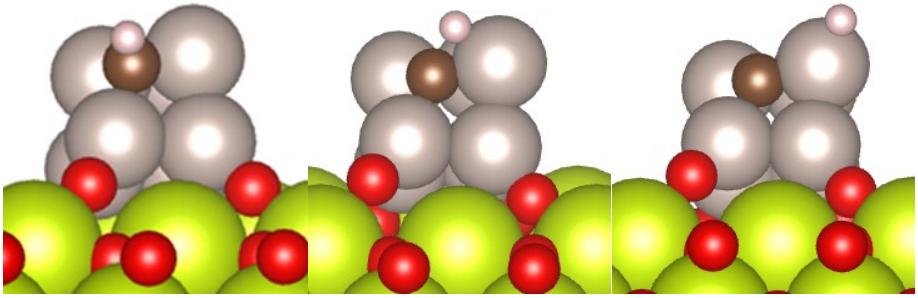
$CH_4^* \rightarrow CH_3^* + H^*$



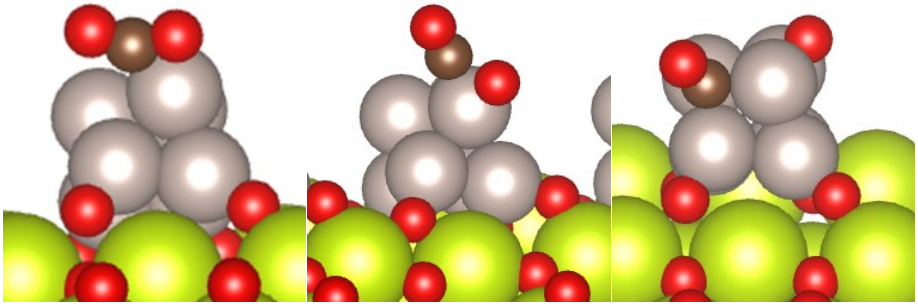
$CH_3^* \rightarrow CH_2^* + H^*$



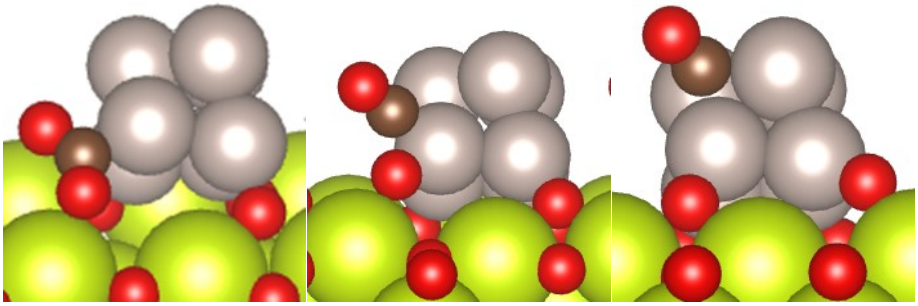
$CH_2^* \rightarrow CH^* + H^*$



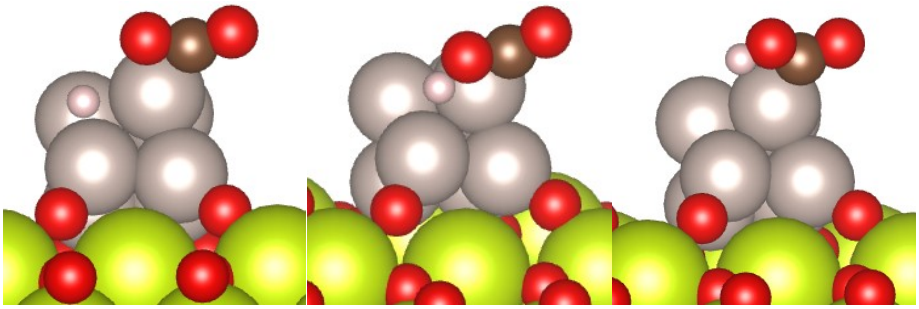
$CH^* \rightarrow C^* + H^*$



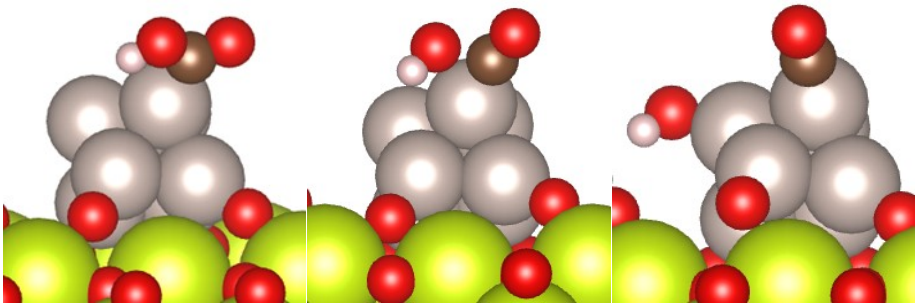
CO_2*→CO*+O*



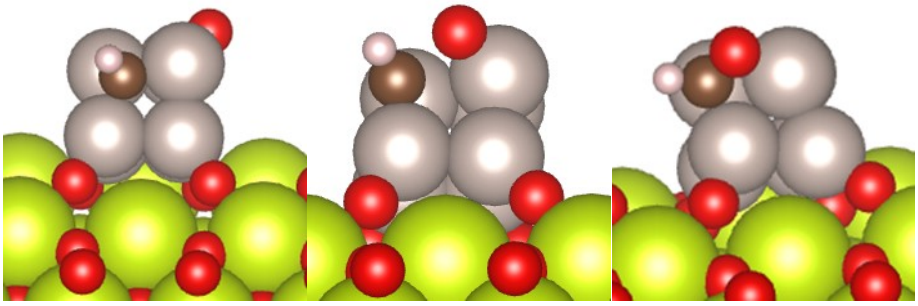
CO_2#→CO*+O#



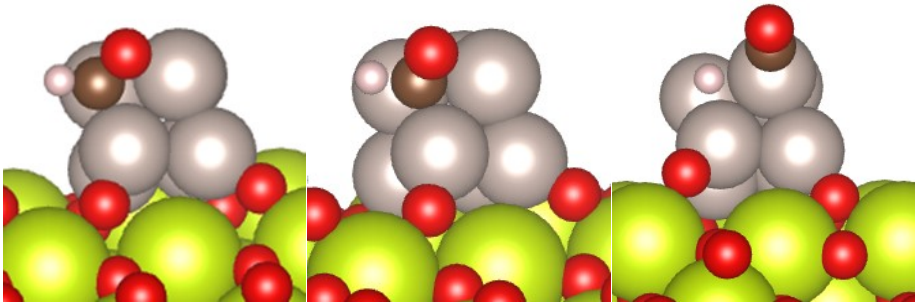
H*+CO_2*→COOH*



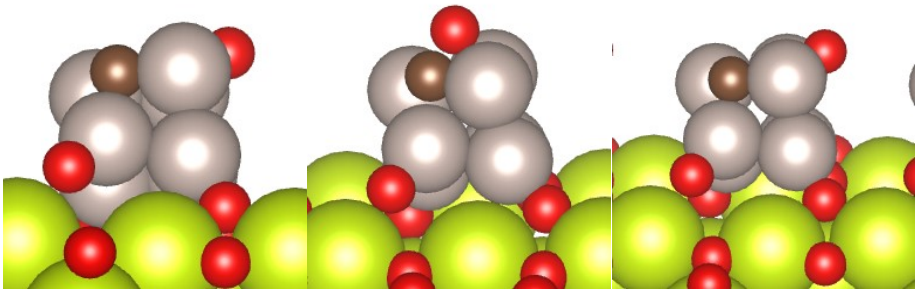
COOH*→CO*+OH*



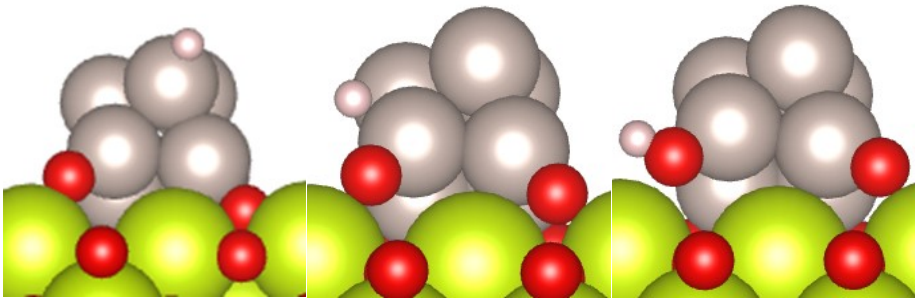
CH*+O*→CHO*



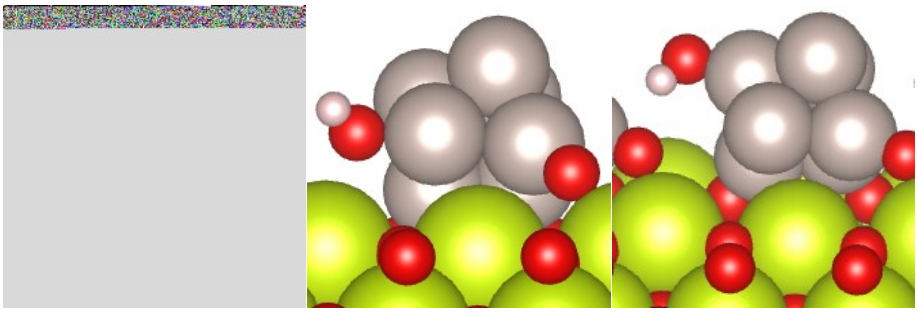
$CHO^* \rightarrow CO^* + H^*$



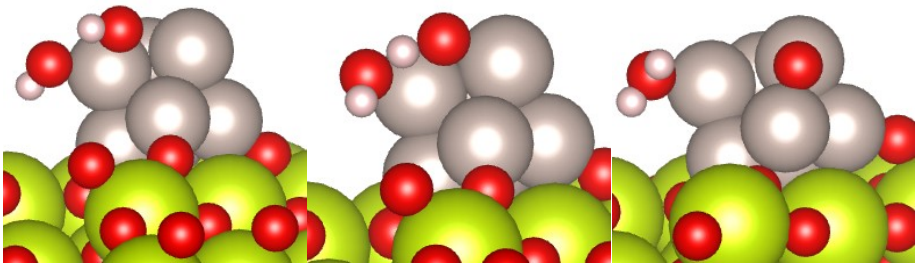
$C^* + O^* \rightarrow CO^*$



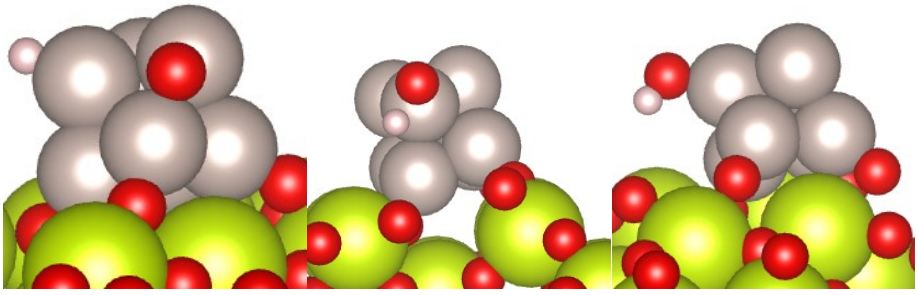
$H^* \rightarrow H\text{-}O_L$



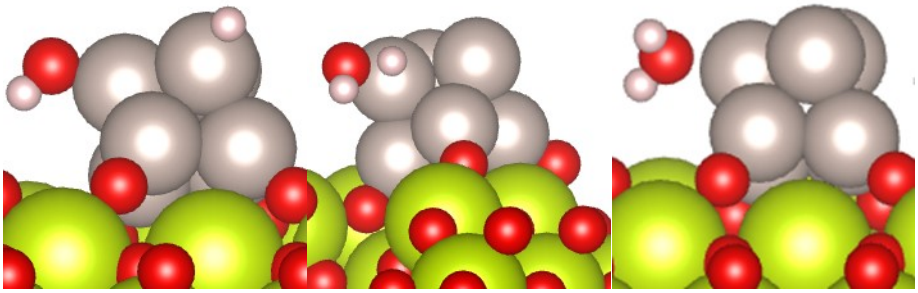
$O_L H \rightarrow OH^*$



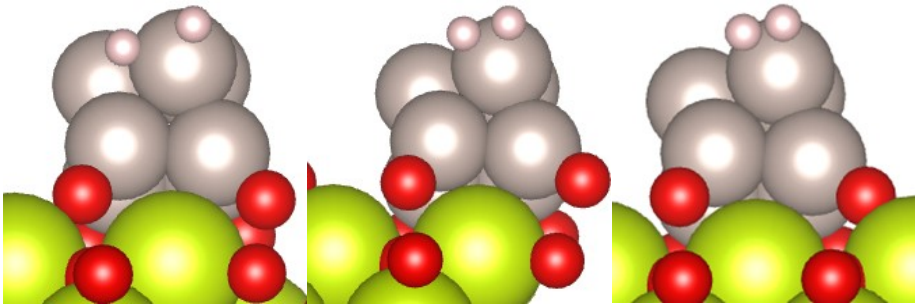
$2OH^* \rightarrow H_2O^* + O^*$



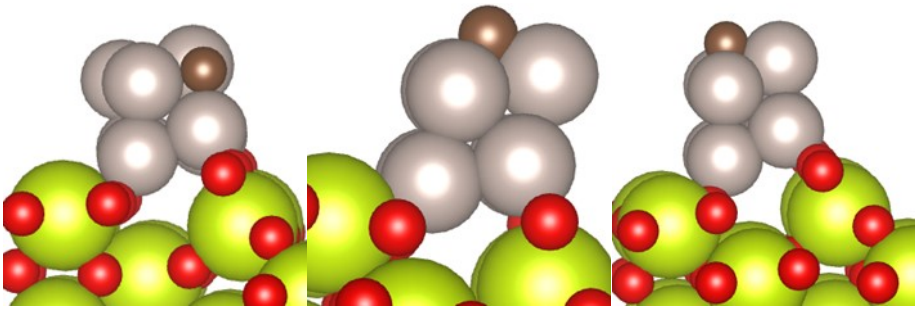
$H^*+O^* \rightarrow OH^*$



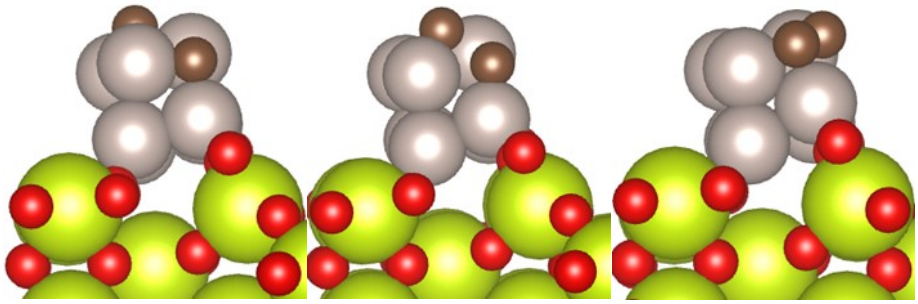
$OH^*+H^* \rightarrow H_2O^*$



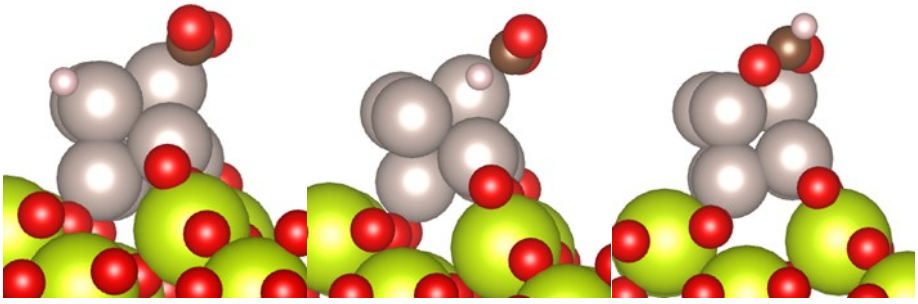
$2H^* \rightarrow H_2^*$



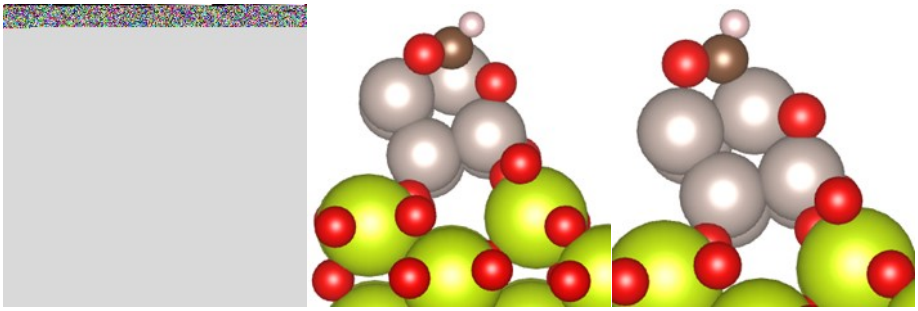
$C^* \rightarrow C^*$



$2C^*\text{-}C \rightarrow C^*$



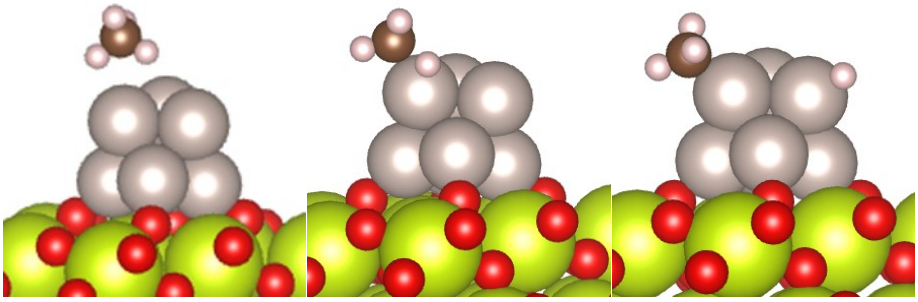
CO_2*+H*→HCOO*



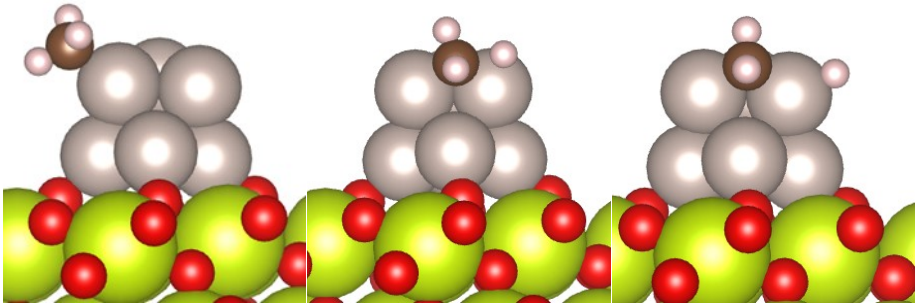
HCOO*→HCO*+O*

HCOO* + H*→HCOOH* (only IS and FS)

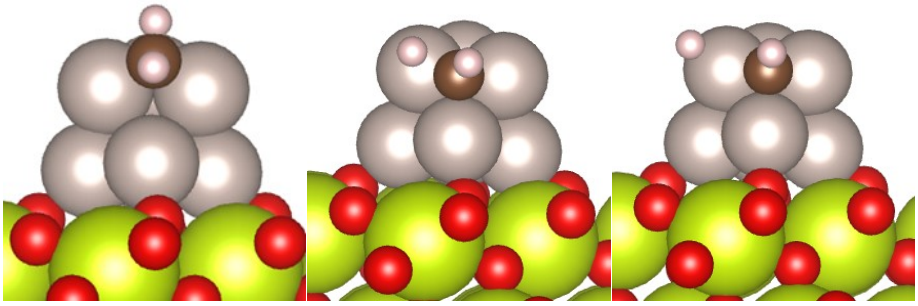
Fig. S9 The IS, TS and FS structure on $Ru_7/CeO_2(110)$



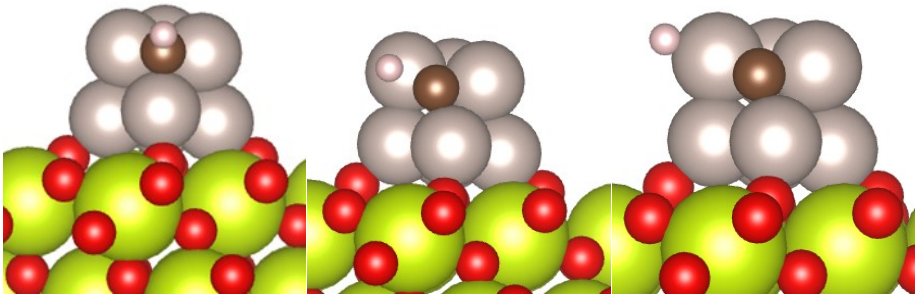
CH_4*→CH_3*+H*



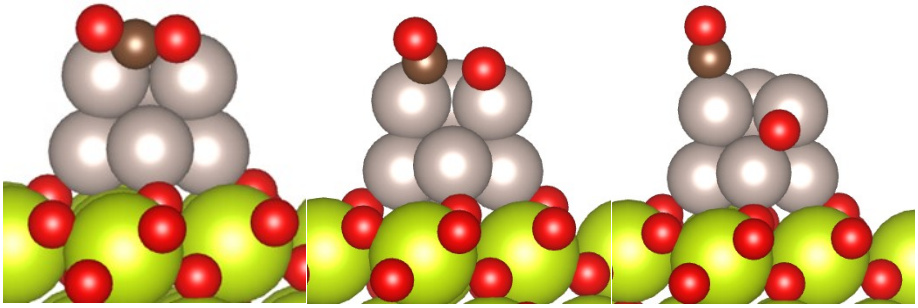
CH_3*→CH_2*+H*



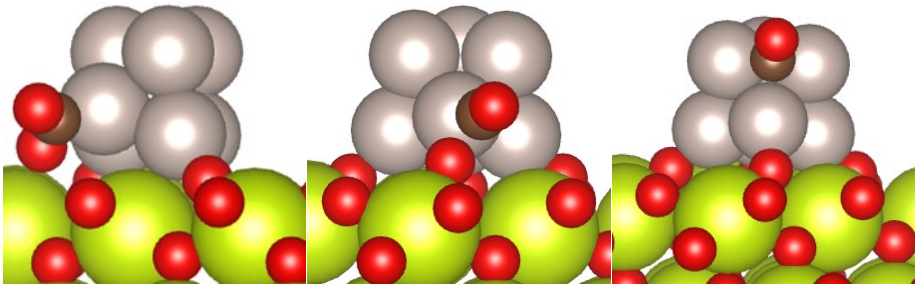
$CH_2^*\rightarrow CH^*+H^*$



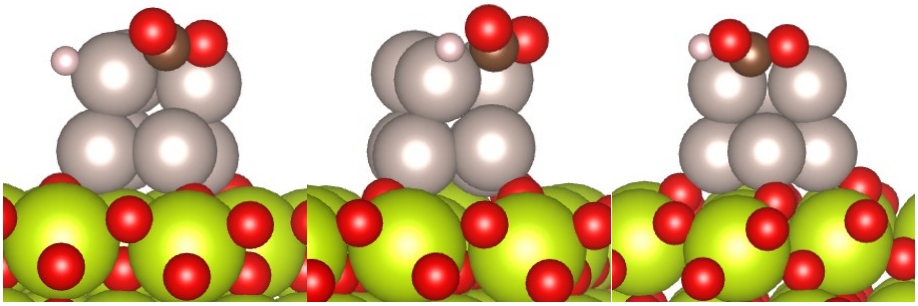
$CH^*\rightarrow C^*+H^*$



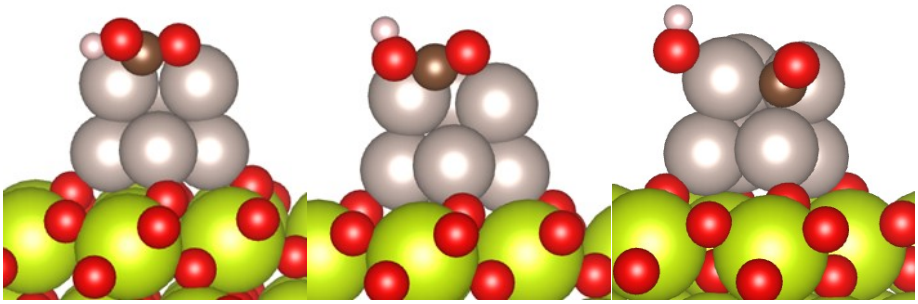
$CO_2^*\rightarrow CO^*+O^*$



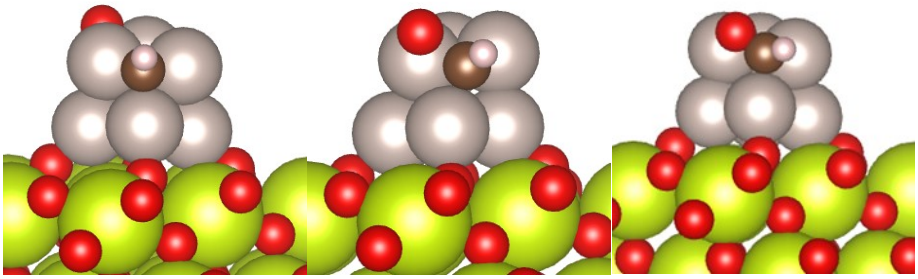
$CO_2\#\rightarrow CO^*+O\#$



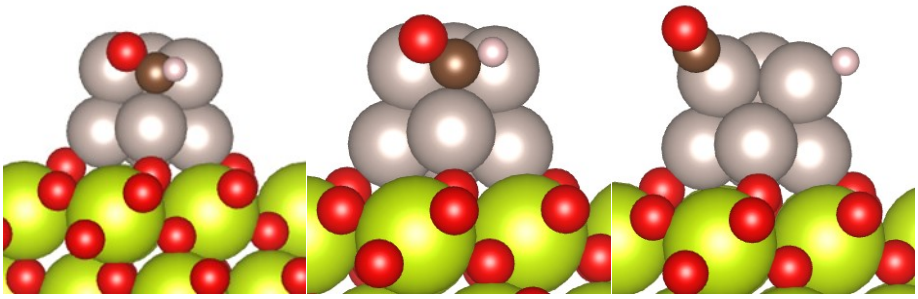
$H^*+CO_2 \rightarrow COOH^*$



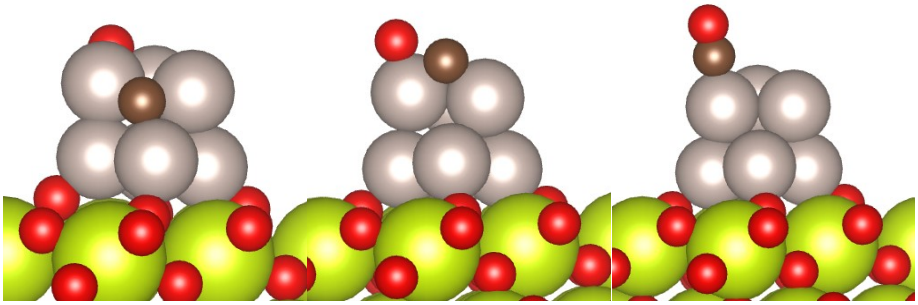
$COOH^* \rightarrow CO^*+OH^*$



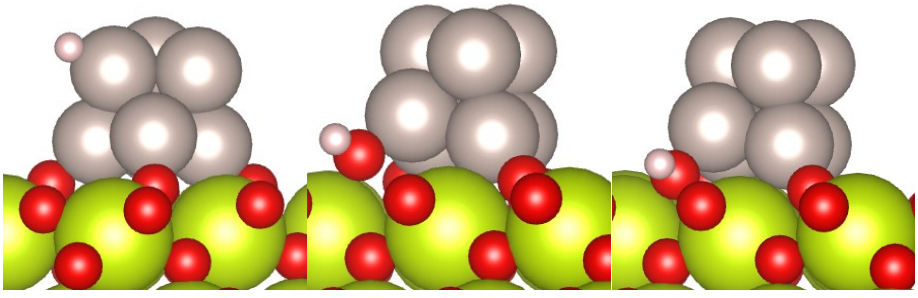
$CH^*+O^* \rightarrow CHO^*$



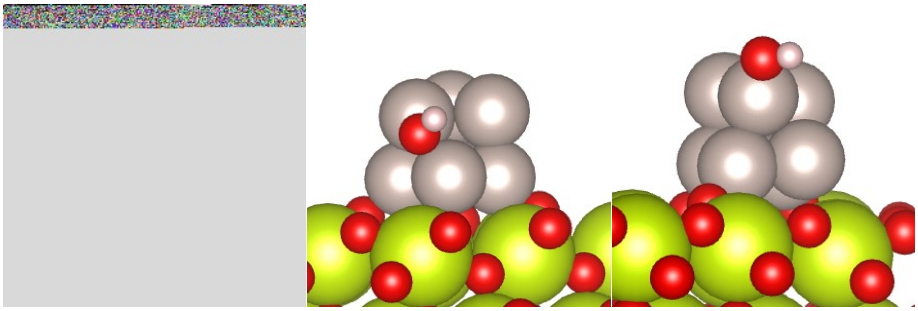
$CHO^* \rightarrow CO^*+H^*$



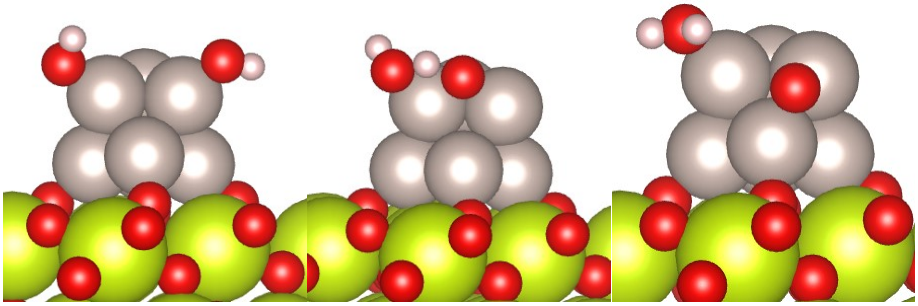
$C^*+O^* \rightarrow CO^*$



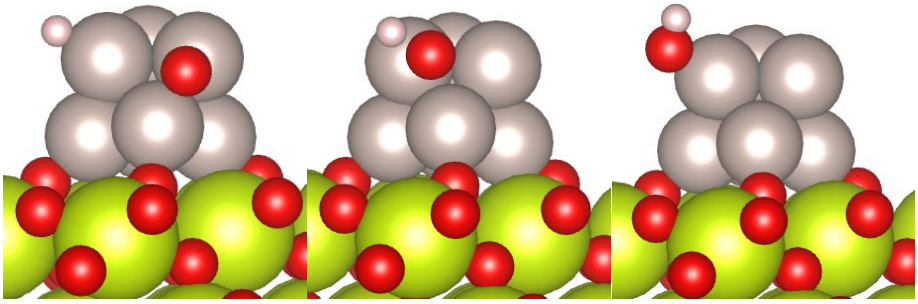
$H^* \rightarrow H\text{-}O_L$



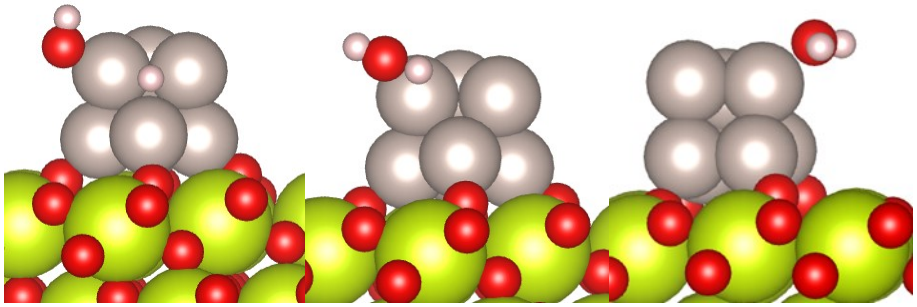
$O_LH \rightarrow OH^*$



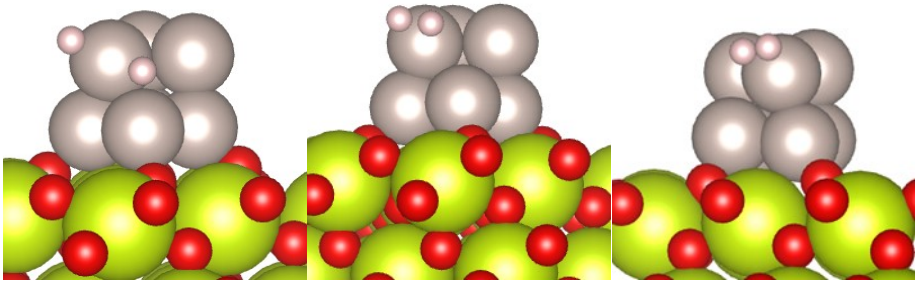
$2OH^* \rightarrow H_2O^* + O^*$



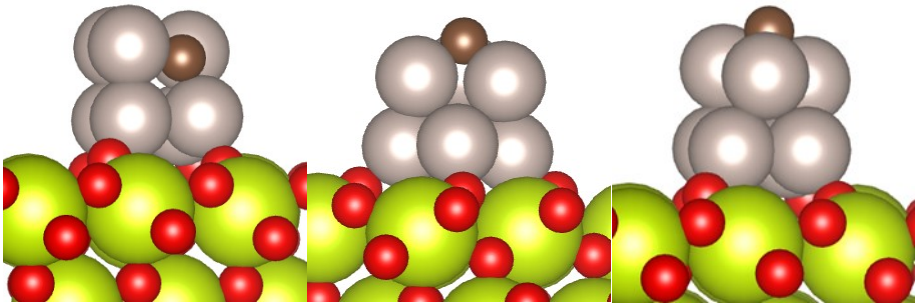
$H^* + O^* \rightarrow OH^*$



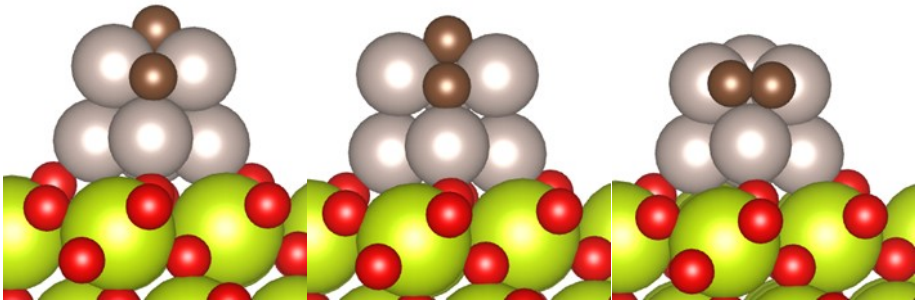
$OH^* + H^* \rightarrow H_2O^*$



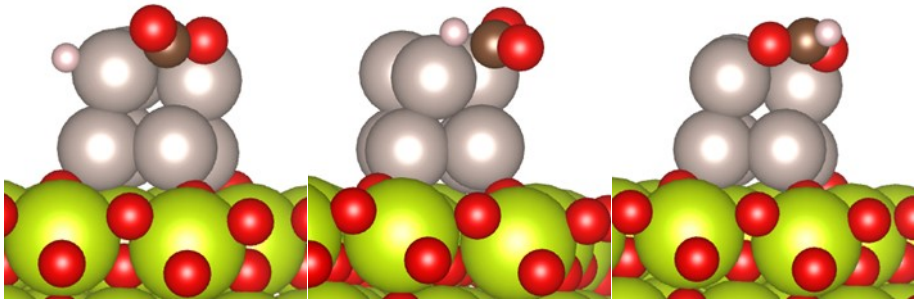
$2H^*\rightarrow H_2^*$



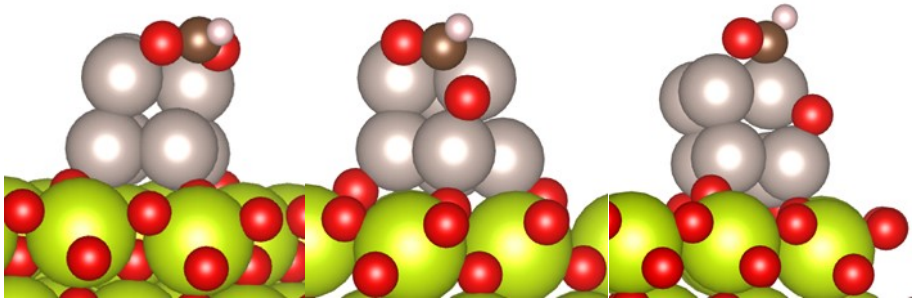
$C^*\rightarrow C^*$



$2C^*\rightarrow C\text{-}C^*$



$CO_2^*+H^*\rightarrow HCOO^*$



$HCOO^*\rightarrow HCO^*+O^*$

Fig. S10 The IS, TS and FS structure on $Ru_7/CeO_2(111)$

Table S1 Calculated adsorption energy (E_{ads}) of the species involved in DRM on $Ru_7/CeO_2(110)$ and $Ru_7/CeO_2(111)$ models

adsorption species	$Ru_7/CeO_2(110)$ (eV)	$Ru_7/CeO_2(111)$ (eV)

CH_4*	-0.64	-0.56
CH_3*	-2.17	-2.55
CH_2*	-4.08	-4.48
CH*	-6.10	-6.45
C*	-7.52	-7.92
CHO*	-2.89	-3.10
OH*	-4.52	-4.53
H*	-2.32	-2.98
H-O_L	-2.57	-2.60
O*	-5.36	-5.56
O#	-6.38	-6.63
H_2O*	-1.62	-0.80
H_2*	-1.02	-0.38
CO	-1.99	-1.39
CO_2#	-0.70	-0.54
CO_2*	-1.15	-0.73
HCOO*	-3.80	-3.92
COOH*	-2.91	-3.24

Table S2 Calculated energetics results of CO_2 hydrogenation steps (unit: eV)

CO_2 hydrogenation steps	**Ru7/CeO2(110)**	**Ru7/CeO2(111)**
	Ea/ΔE	Ea/ΔE
CO2* + H*→HCOO*	0.60/-0.85	0.54/-0.58
HCOO* → HCO* + O*	1.69/1.05	1.76/0.92
HCOO* + H* → HCOOH*	—/1.55	—/—
CO2* + H*→COOH*	1.78/0.55	1.45/0.09
COOH*→CO*+OH*	0.40/-1.63	0.50/-1.48

Table S3 Calculated energetics results of C* diffusion and C-C coupling (unit: eV)

CO_2 hydrogenation steps	**Ru_7/CeO_2(110)**	**Ru_7/CeO_2(111)**
	Ea/ Δ E	Ea/ Δ E
C*, diffusion	0.68/0.42	2.20/1.78
2C*→C-C*	1.39/-0.56	0.89/-0.55

Table S4 Calculated Net Rates of Reactions at 1000K and 1atm

Reaction steps of DRM	**Net Rate of Reaction ($site^{-1}$ s^{-1})**	
	Ru_7/CeO_2(110)	Ru_7/CeO_2(111)
2*_s + CH4_g <-> H-CH3* + *_s -> CH3* + H*	0.00060	$2.60x10^{-8}$
_s + CH3* <-> H-CH2* + *_s -> CH2* + H	0.00060	$2.60x10^{-8}$
_s + CH2* <-> H-CH* + *_s -> CH* + H	0.00060	$2.60x10^{-8}$
_s + CH* <-> H-C* + *_s -> C* + H	$9.67x10^{-8}$	$1.73x10^{-16}$
***_s + #_s + CO2_g <-> O-CO# + *_s -> CO* + O_L**	0.00077	$2.60x10^{-7}$
CO2_g + H* <-> H-COO* -> COOH*	$1.95x10^{-10}$	$2.51x10^{-14}$
COOH* + *_s <-> CO-OH* + *_s-> CO* + OH*	$1.95x10^{-10}$	$2.51x10^{-14}$

O_L + H* <-> H-O_L + H* -> O_LH* + #_s	0.00077	$2.60x10^{-7}$
OH* + *_s <-> O-H* + *_s -> O* + H*	0.0006	$2.60x10^{-7}$
OH* + H* <-> H-OH* + *_s <-> H2O* + *_s	0.00016	$4.94x10^{-13}$
CH* + O* <-> O-CH* + *_s -> CHO* + *_s	0.00060	$2.60x10^{-7}$
C* + O* <-> O-C* + *_s -> CO* + *_s	$9.67x10^{-8}$	$1.73x10^{-16}$
CHO* + *_s <-> H-CO* + *_s -> CO* + H*	0.00060	$2.60x10^{-7}$
CO* -> CO_g + *_s	0.00137	$5.20x10^{-7}$
H2O* -> H2O_g + *_s	0.00016	$4.94x10^{-13}$
2H* <-> H-H* + *_s -> H2_g + 2*_s	0.00104	$5.20x10^{-7}$

Table S5 Calculated Net Rates of Reactions including C-C coupling at 1000K and 1atm

Reaction steps of DRM	Net Rate of Reaction ($site^{-1}$ s^{-1})
	$Ru_7/CeO_2(110)$
2*_s + CH4_g <-> H-CH3* + *_s -> CH3* + H*	$7.81x10^{-5}$
_s + CH3 <-> H-CH2* + *_s -> CH2* + H*	$7.81x10^{-5}$
_s + CH2 <-> H-CH* + *_s -> CH* + H*	$7.81x10^{-5}$
_s + CH <-> H-C* + *_s -> C* + H*	$2.65x10^{-5}$
2C* <-> C-C* + *_s -> C2* + *_s	$4.83x10^{-87}$
*_s + #_s + CO2_g <-> O-CO# + *_s -> CO* + O_L	$7.82x10^{-5}$
CO2_g + H* <-> H-COO* -> COOH*	$1.65x10^{-11}$
COOH* + *_s <-> CO-OH* + *_s-> CO* + OH*	$1.65x10^{-11}$
O_L + H* <-> H-O_L + H* -> O_LH* + #_s	$7.82x10^{-5}$
OH* + *_s <-> O-H* + *_s -> O* + H*	$7.81x10^{-5}$
OH* + H* <-> H-OH* + *_s <-> H2O* + *_s	$1.23x10^{-7}$
CH* + O* <-> O-CH* + *_s -> CHO* + *_s	$5.15x10^{-5}$
C* + O* <-> O-C* + *_s -> CO* + *_s	$2.65x10^{-5}$
CHO* + *_s <-> H-CO* + *_s -> CO* + H*	$5.15x10^{-5}$
CO* -> CO_g + *_s	0.00016
H2O* -> H2O_g + *_s	$1.23x10^{-7}$
2H* <-> H-H* + *_s -> H2_g + 2*_s	0.00016

Note: Ru7/CeO2(111) is deactivation by C-C coupling and not has reaction rate.

Table S2. Calculated energetics results of elementary reactions involved in methane reforming reaction network on $Ru_7/CeO_2(110)$ and $Ru_7/CeO_2(111)$ models (unit: eV)

Reaction steps of DRM	$Ru_7/CeO_2(110)$	$Ru_7/CeO_2(111)$
	$E_a/\Delta E$	$E_a/\Delta E$
$CH_{4(g)} \rightarrow CH_3$*+H*	0.29/-0.41	0.58/-0.04
CH3*→ CH2*+H*	0.63/0.16	0.50/0.34
CH2*→ CH*+H*	0.27/-0.53	0.39/-0.51
CH*→C*+H*	0.67/0.12	0.55/-0.28
CO2*→CO*+O*	1.32/-0.27	1.14/0.53
CO2_v→CO*+O_v	0.69/-1.20	0.27/-1.73
CO2*+H*→COOH*	1.78/0.55	1.45/0.09
COOH*→CO*+OH*	0.40/-1.63	0.50/-1.48

CH*+O*→CHO*	0.99/-0.46	1.40/-0.05
CHO*→CO*+H*	0.50/-0.53	0.56/-0.60
C*+O*→CO*	2.65/-0.85	4.83/-0.05
2OH*→H2O*+O*	0.31/-0.31	0.73/-0.48
O*+H*→OH*	1.32/-0.93	1.05/-0.98
OH*+H*→H2O*	1.43/0.47	2.02/1.05
2H*→H2*	0.54/0.23	0.63/0.47