Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting information

## Revealing the catalytic role of $CO_2$ in propane dehydrogenation on chromium oxide catalyst

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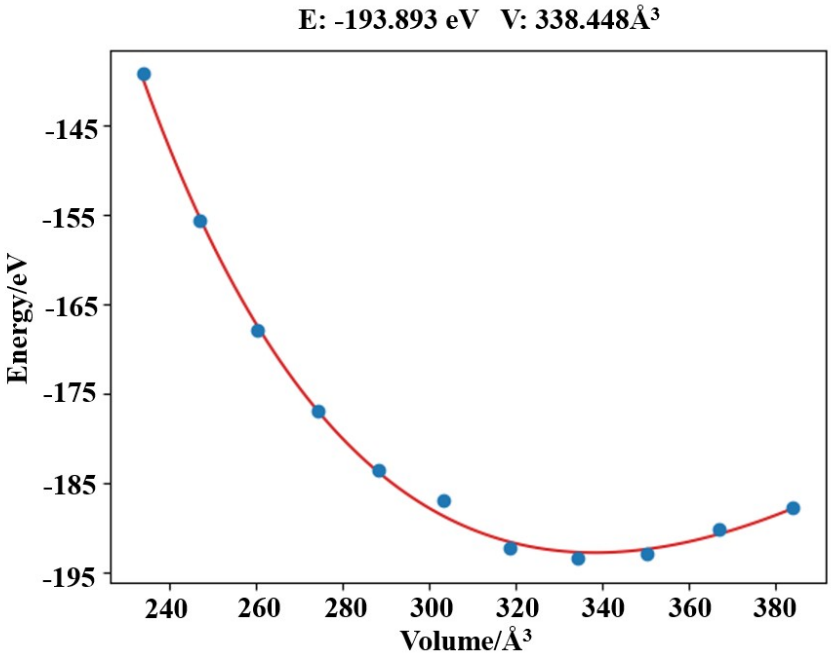
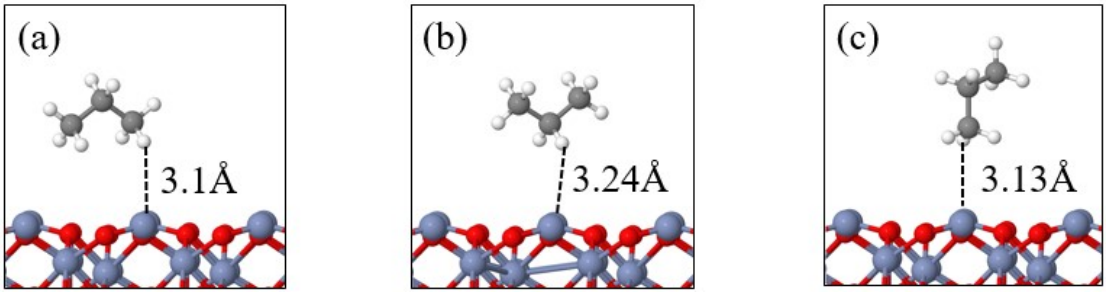
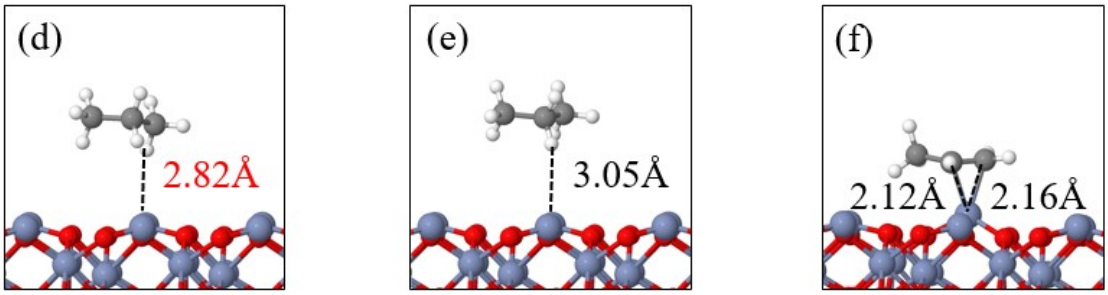



Figure S1. Schematic diagram of the relationship between the volume and energy to calculate the lattice constant in the $Cr_2O_3$ bulk.




$E_{ads}$=-0.26eV $E_{ads}$=-0.22V $E_{ads}$=-0.24eV




$E_{ads}$=-0.33eV $E_{ads}$=-0.26eV $E_{ads}$=-0.97eV

Figure S2. The adsorption energy and configurations of (a-e) $C_3H_8$ and (f) $C_3H_6$ . The distance between adsorbed molecule and binding site is indicated. Color code: White: H, Gray: C.

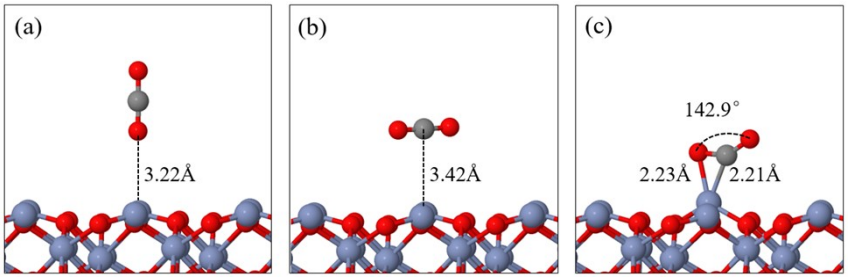



Figure S3. The configurations of $CO_2$ adsorbed on the $Cr_2O_3$ (a), (b) physisorption; (c) chemisorption.

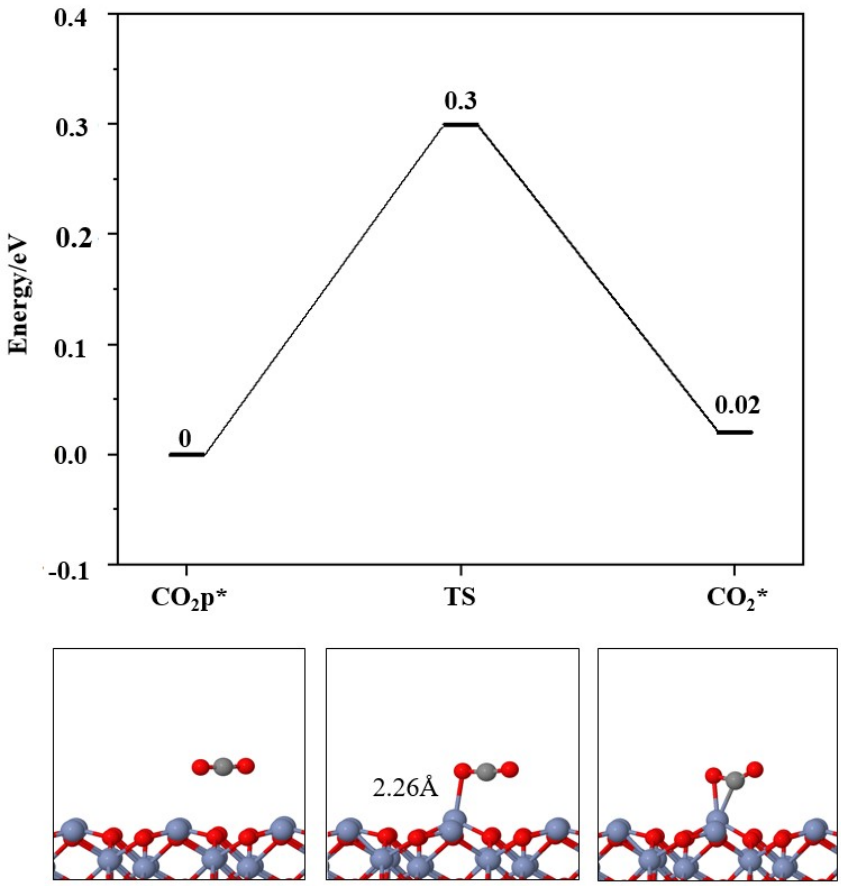



Figure S4. The reaction pathway of the transition from $CO_2$ in physisorption to the chemisorption.

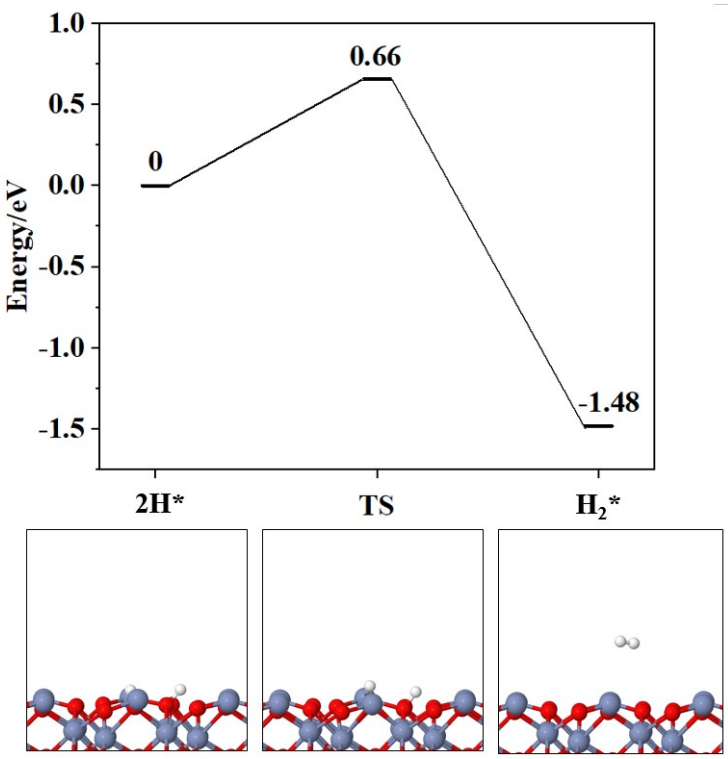
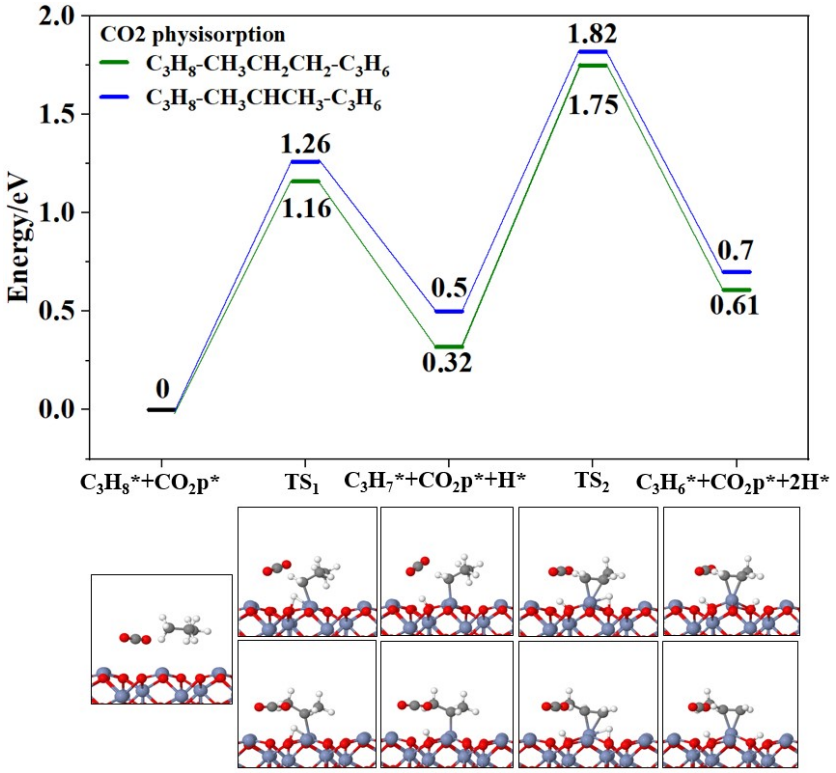



Figure S5. The reaction pathway of the hydrogen molecule formation.


CO2 physisorption
C3H8-CH3CH2CH2-C3H6
C3H8-CH3CHCH3-C3H6
Energy/eV
2.0
1.5
1.0
0.5
0.0
0
1.26
1.16
0.5
0.32
1.82
1.75
0.7
0.61
C3H8*+CO2p*
TS1
C3H7*+CO2p*+H*
TS2
C3H6*+CO2p*+2H*

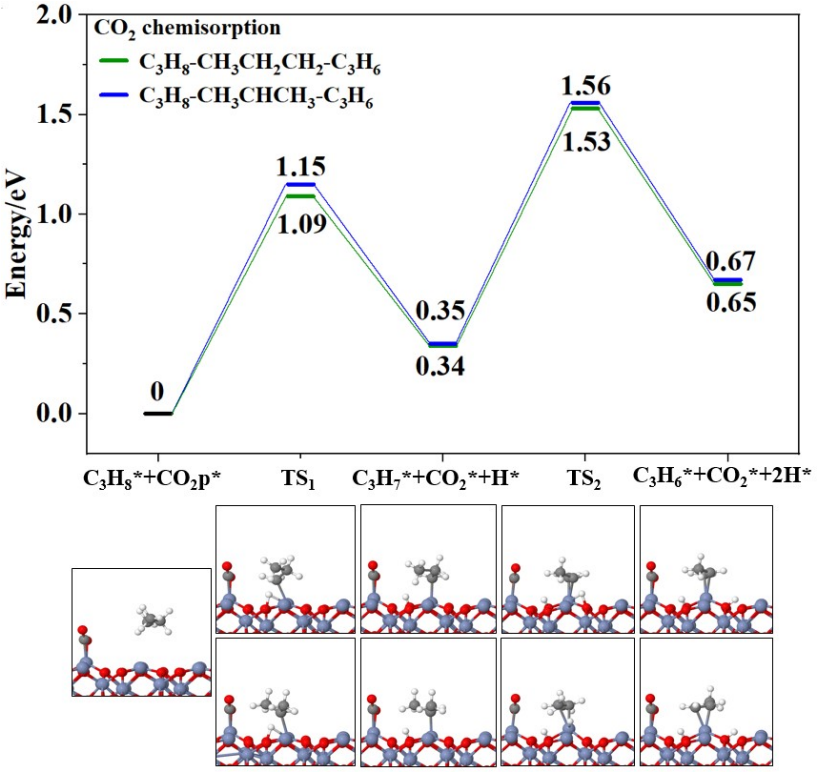

CO2 chemisorption
C3H8-CH3CH2CH2-C3H6
C3H8-CH3CHCH3-C3H6
Energy/eV
2.0
1.5
1.0
0.5
0.0
0
1.15
1.09
0.35
0.34
1.56
1.53
0.67
0.65
C3H8*+CO2p*
TS1
C3H7*+CO2*+H*
TS2
C3H6*+CO2*+2H*

Figure S6. The reaction pathways and important configurations of propane dehydrogenation under $CO_2$ physisorption and chemisorption respectively.

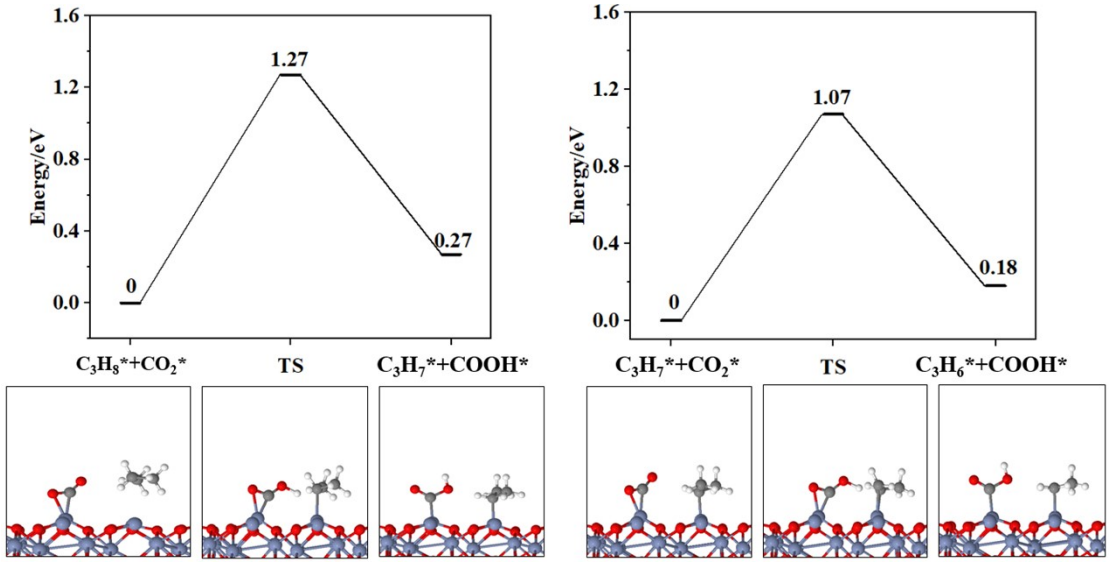



Figure S7. The reaction pathway of hydrogen abstraction from $C_3H_8$ and $C_3H_7$ by adsorbed $CO_2$.

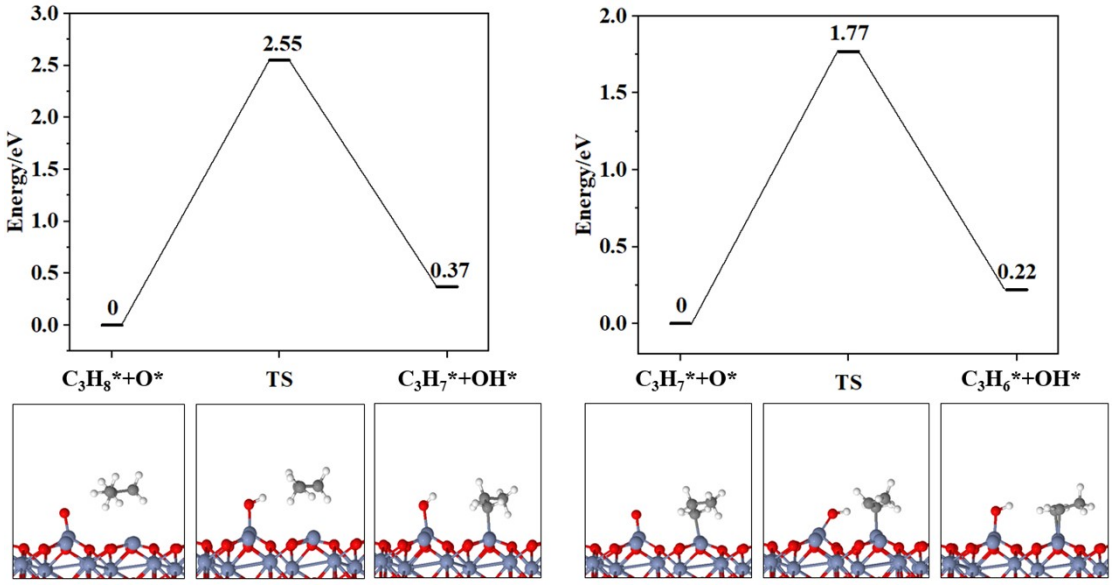



Figure S8. The reaction pathway of hydrogen abstraction from $C_3H_8$ and $C_3H_7$ by adsorbed oxygen (O*).

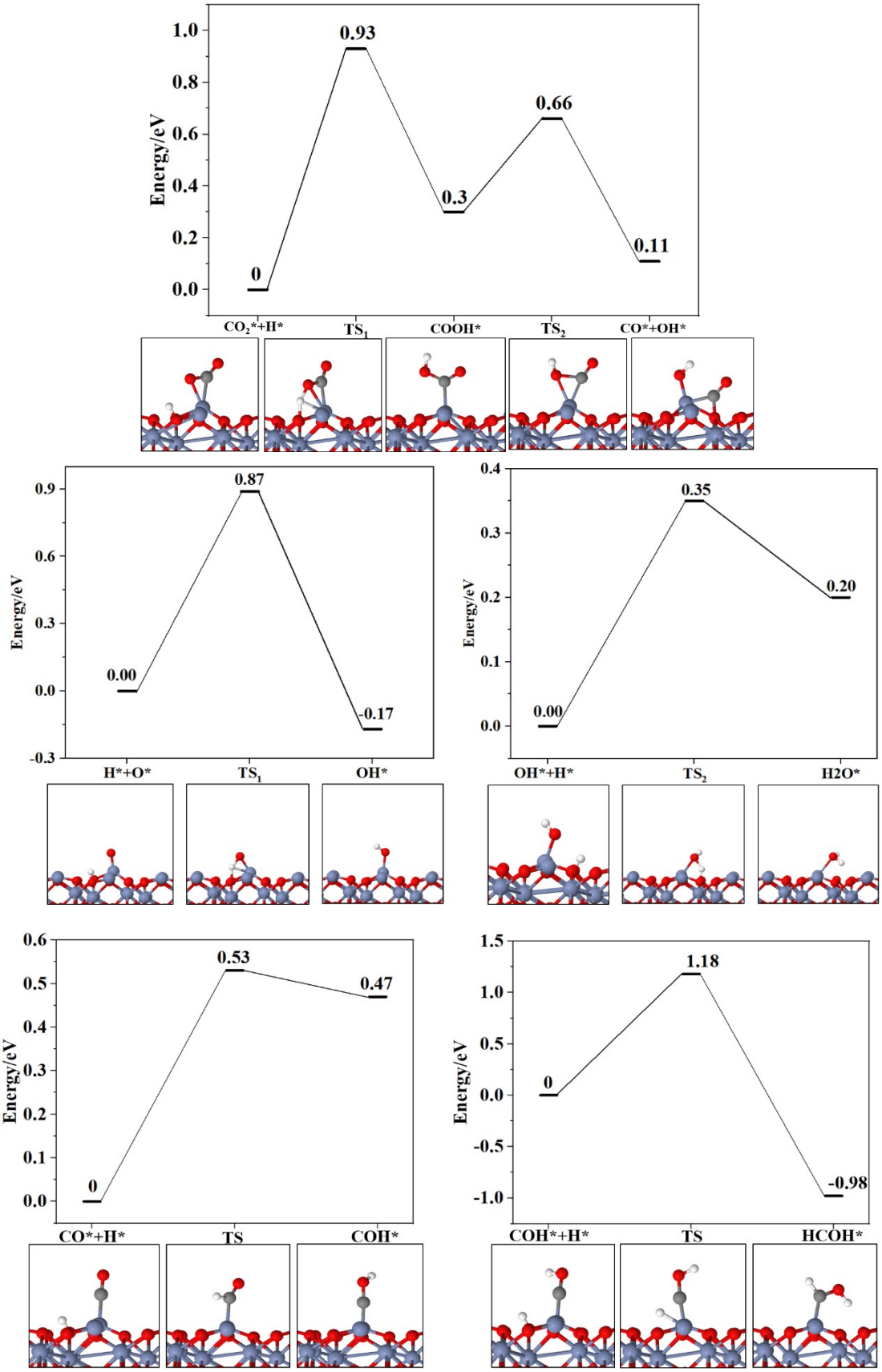



Figure S9. The reaction pathway of removal of surface hydroxyl by (a) $CO_2$, (b) CO* and (c) O* respectively.

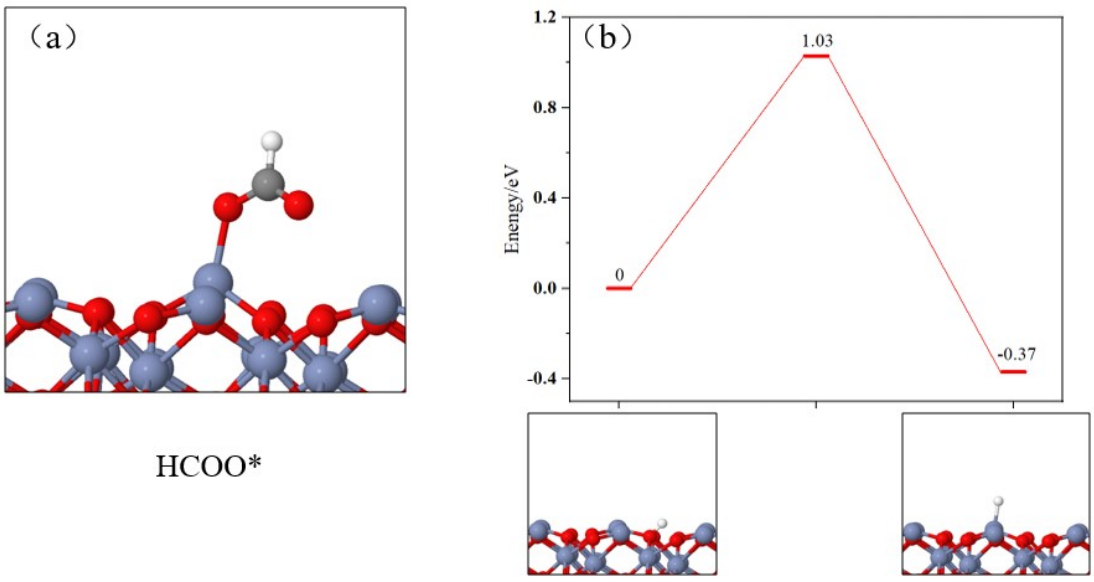



Figure S10. (a) The optimized structure of adsorbed HCOO* (b) The diffusion pathway of hydrogen from O site to Cr site.

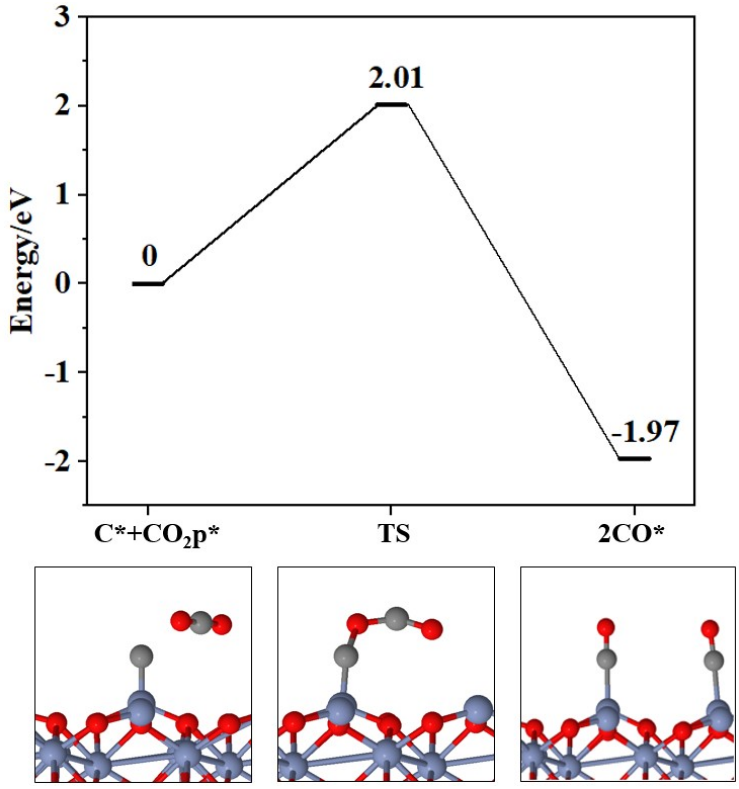



Figure S11. The reaction pathway of reverse Boudard reaction.

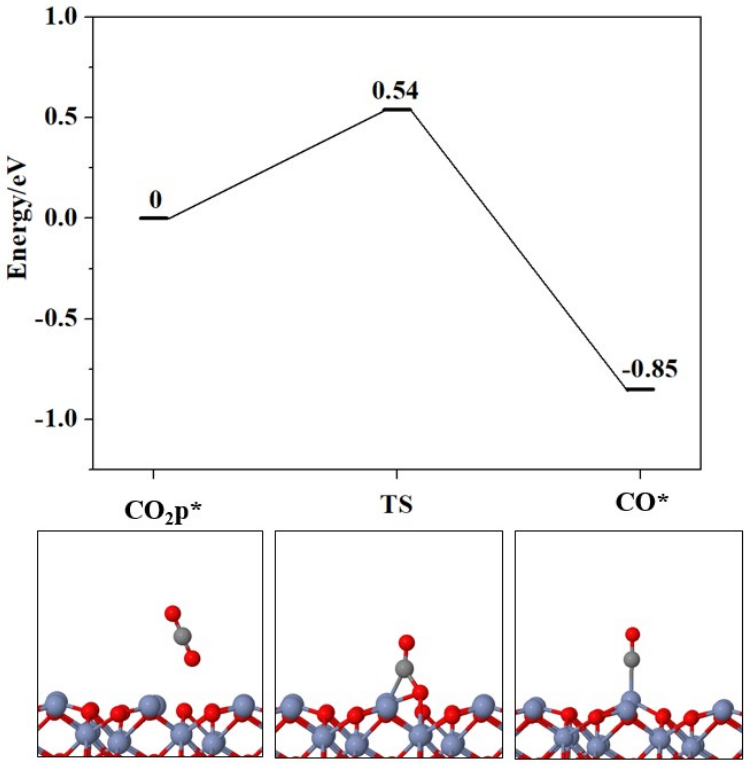



Figure S12. The reaction pathway of the filling of oxygen vacancy by $CO_2$.

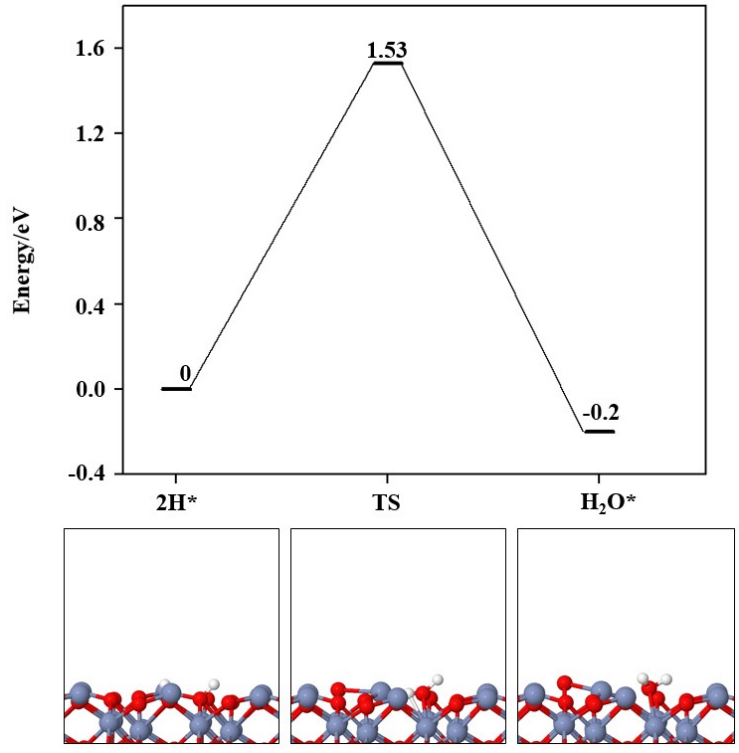



Figure S13. The reaction pathway of the water formation from the surface hydroxyls.

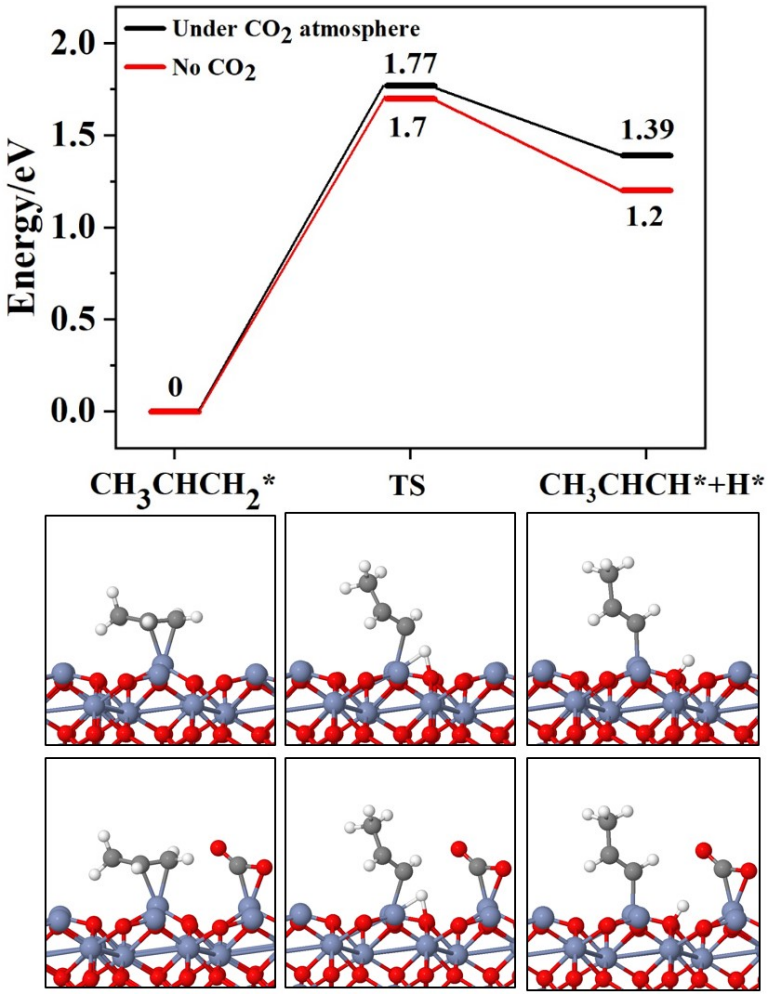



Figure S14. The reaction pathway of propene dehydrogenation with/without $CO_2$.

**Table S1. The calculated adsorption energy at 0 and 800 K of propane and propene.**

| Temperature | Propane | Propene |
|---|---|---|
| 0 K | -0.33 eV | -0.97 eV |
| 800 K | -0.37 eV | -0.46 eV |

**Table S2. The coverage of all adsorptive species on the surface of $Cr_2O3$ under different partial pressure at 800K. (The * represents the adsorptive species )**

| Adsorptive species | $C_3H_8/CO_2$=1:2 | $C_3H_8/CO_2$=1:1 | $C_3H_8/CO_2$=2:1 |
|---|---|---|---|
| $CH_3CH_2CH_3$* | 9.63E-10 | 1.44E-09 | 1.93E-09 |
| $CH_3CH_2CH_2$* | 4.32E-09 | 6.48E-09 | 8.64E-09 |
| $CH_3CHCH_2$* | 4.83E-15 | 7.24E-15 | 9.65E-15 |
| $CO_2$* | 5.70E-10 | 4.28E-10 | 2.85E-10 |
| $CO_2$p* | 7.71E-10 | 5.78E-10 | 3.85E-10 |
| $H_2O$* | 3.40E-20 | 5.05E-20 | 6.67E-20 |
| CO* | 2.94E-07 | 2.21E-07 | 1.47E-07 |
| CO*-O | 3.91E-21 | 1.37E-21 | 9.45E-22 |

| | | | |
|---|---|---|---|
| COH*-O* | 1.01E-22 | 3.52E-23 | 2.44E-23 |
| OH* | 2.07E-10 | 2.51E-10 | 2.88E-10 |
| O* | 1.17E-05 | 1.17E-05 | 1.17E-05 |
| C* | 1.68E-06 | 2.05E-06 | 2.37E-06 |
| $CH_3CHCH_3$* | 2.75E-07 | 3.10E-07 | 2.77E-07 |
| $H_2$* | 2.37E-09 | 3.56E-09 | 4.75E-09 |
| $H_2Ov$* | 1.10E-19 | 1.64E-19 | 2.19E-19 |
| $CO_2$* | 9.01E-22 | 1.35E-21 | 1.80E-21 |
| COH* | 9.52E-11 | 8.75E-11 | 6.73E-11 |
| HCOH* | 2.19E-10 | 2.46E-10 | 2.19E-10 |
| COOH* | 4.24E-18 | 3.86E-18 | 2.94E-18 |
| COO-vo* | 3.12E-13 | 2.34E-13 | 1.56E-13 |